

## Spatial scale dependence of self-diffusion in molecular and ionic liquids

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The self-diffusion of a molecule in a liquid is believed to follow the Fick's law. In the case, the self-part of the van Hove correlation function decays exponentially in time (Debye relaxation) and is a Gaussian in space. As a consequence, the variation of relaxation time  $\tau$  in a momentum transfer  $Q$  can be described as  $\tau(Q) = D^{-1}Q^{-2}$  ( $D$ : self-diffusion coefficient). A question arises as to whether the relation  $\tau \propto Q^{-2}$  is still valid in the case the relaxation is of non-Debye type. In fact, the non-Debye relaxation is often observed in glass-forming liquids. To address the issue, we have investigated the diffusion dynamics of two types of glass-forming liquids by means of an incoherent quasielastic neutron scattering (QENS) technique which can probe the microscopic nature of the diffusion process.

The materials chosen in this work are a molecular liquid, 3-methylpentane (3MP), and an ionic one, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C4mimTFSI). Both materials involve hydrogen atoms with a huge incoherent scattering cross section. The incoherent QENS measurements were carried out using NSE, HFBS and DCS spectrometers at NIST in USA.

The obtained relaxation curves were fitted with the Kohlrausch-Williams-Watts (KWW) stretched exponential function,  $\exp\{-(t/\tau)^\beta\}$  ( $0 < \beta \leq 1$ ). Figure 1 displays the  $Q$ -dependence of the relaxation time,  $\tau$ , and the stretching parameter,  $\beta$ , for 3MP. The solid and dashed lines denote the  $\tau \propto Q^{-2}$  behavior. Obviously,  $\tau$  and  $\beta$  have kinks at  $Q_1$  ( $\approx 0.2 \text{ \AA}^{-1}$ ) and  $Q_2$  ( $\approx 0.6 \text{ \AA}^{-1}$ ). At  $Q < Q_1$  (the hydrodynamic limit), the relaxation is of Debye type ( $\beta = 1$ ) and its characteristic time is proportional to  $Q^{-2}$ , indicating that the Fickian diffusion occurs.

In the region  $Q_1 < Q < Q_2$ ,  $\tau$  changes with  $Q$  more steeply and  $\beta$  varies between 1 and 0.5. At  $Q > Q_2$ ,  $\tau$  is again proportional to  $Q^{-2}$  and  $\beta$  reaches a constant value of 0.5. Similar behavior is also observed for C4mimTFSI. This is the first clear experimental demonstration of double crossovers in both  $\tau(Q)$  and  $\beta(Q)$ .

Given that the particle has a memory of its previous position, the relaxation exhibits the stretched exponential behavior. At small spatial scale ( $Q > Q_2$ ) or at short times, the particle undergoes only a few steps with the strong memory effect. While, in the low  $Q$  ( $< Q_1$ ) or in the long time limit, the particle completely loses the memory and its motion resembles the random walk (Fickian process). In the intermediate region ( $Q_1 < Q < Q_2$ ), the particle dynamics is transient; the particle gradually loses the memory. It should be mentioned that the crossover at  $Q_2$  is interpreted as the crossover from the Gaussian behavior at lower  $Q$  to the non-Gaussian one at higher  $Q$  [1, 2], which is associated with the "spatial averaging" of the particle motion.

So far, the crossovers have been reported only for glycerol [1] and polymers [1]. There are several types of glasses, i.e., network glass, molten salt glass, molecular glass, metallic glass, and polymer glass. Our present work demonstrated that the crossovers in  $\tau(Q)$  and  $\beta(Q)$  is a generic feature for glass-forming liquids.

### References

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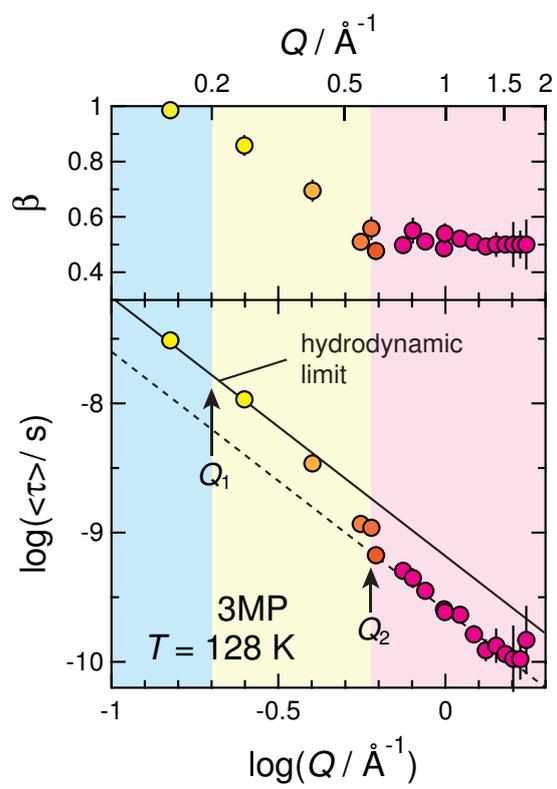


Fig. 1. Relaxation time and a stretching parameter as a function of  $Q$  for 3MP.