Electronic Supplementary Information for

Time scale of dynamic heterogeneity in model ionic liquids and its relation to static length scale and charge distribution

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Method of $\Delta\phi(t', t'')$ calculation

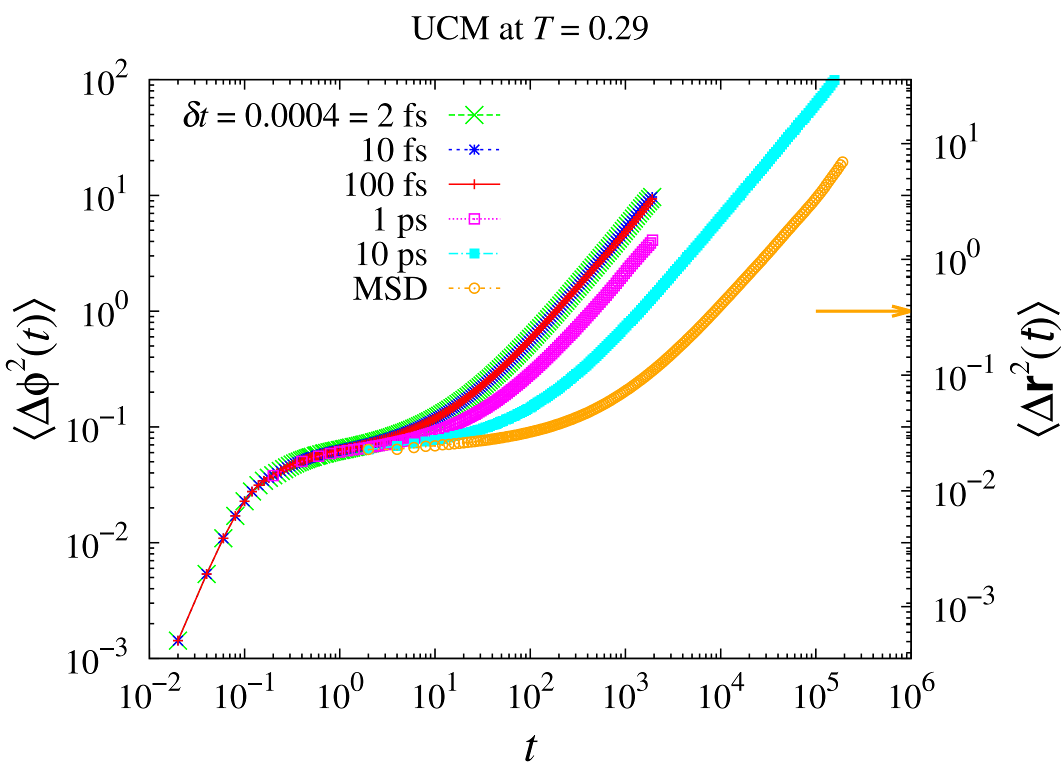

Fig. S1 MSAD of UCM at $T = 0.29$. $\delta t = 2$ fs (green), 10 fs (blue), 100 fs (red), 1 ps (magenta), and 10 ps (cyan). The first thee curves collapse. For comparison the MSD of translational motion is plotted with the orange curve.

For calculating the MSAD, we made a trajectory saved every time step, $dt = 0.0004$ or 2 fs, the time step for MD integrator, thus the shortest time interval, but at low temperatures we took longer time intervals, δt,

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for the $\Delta\boldsymbol{\phi}$ integration, for example, we used 100 fs for δt at $T = 0.29$ UCM.

The angular displacement of j-th cation from $t = t'$ to t'' is calculated with

$$\Delta\boldsymbol{\phi}_j(t',t'') = \int_{t'}^{t''} dt\,\boldsymbol{\omega}_j(t) = \sum_{k=0}^{n-1} \delta t\,\boldsymbol{\omega}_j(t'+k\delta t), \tag{1}$$

where

$$\boldsymbol{\omega}_j(t) = \frac{\mathbf{r}_j^{(\mathrm{rel})}(t)\times\mathbf{v}_j^{(\mathrm{rel})}(t)}{d_j^2} \tag{2}$$

is the instantaneous angular velocity of the j-th cation, and $t''-t' = n\delta t$, and $\mathbf{r}_j^{(\mathrm{rel})}(t)$ and $\mathbf{v}_j^{(\mathrm{rel})}(t)$ are the position and the velocity of the reduced mass of the j-th cation at time t, and d_j is its bond length.

With longer δt ($> dt = 2$ fs), we used the alternate equation,

$$\Delta\boldsymbol{\phi}_j(t',t'') = \sum_{k=0}^{n-1} \delta t\,\overline{\boldsymbol{\omega}}_j(t'+k\delta t), \tag{3}$$

where

$$\overline{\boldsymbol{\omega}}_j(t) = \frac{\hat{\mathbf{u}}_j(t)\times\hat{\mathbf{u}}_j(t+\delta t)}{\delta t} \tag{4}$$

is the average angular velocity during δt, where $\hat{u}_j(t)$ is the orientational vector of the $j-$th cation at time t. With $\delta t = dt$, the Eq. (4) becomes Eq. (2), and the two Eqs. are equivalent.

Dependence of the time interval on $\Delta\boldsymbol{\phi}(t',t'')$

Fig. S1 is the plot of MSAD of UCM at $T = 0.29$ with $\delta t = 2$ fs (green), 10 fs (blue), 100 fs (red), 1 ps (magenta), and 10 ps (cyan), and the three shortest δt cases overlap with each other. With the longer δt (≥ 1 ps) the MSAD shows longer subdiffusive regime. The stacking of small angular displacements in librational motion contributes less with the longer δt, and it takes more time for it to reach diffusive regime.

We used the MSAD results with $\delta t = 100$ fs at the lowest temperature for all the systems in this study. Although D_{R} is estimated smaller with longer δt, the MSAD results with $\delta t \leq 100$fs are believed to be reliable.

The DSE relations in our systems break down much more severely than the breakdown of the SE relation at low temperatures (see Figs. 6(d) to 6(f) in the main text). Because τ_{R} is calculated correctly, we suspect that D_{R} is calculated much greater than expected from the DSE relation, compared to the amount of decoupling in translational SE relation. We would have obtained less severe decoupling of DSE relation with less D_R if we had used coarser time intervals, $\delta t \geq 1$ ps, of integration.

With the finest δt at all temperatures, however, we would not obtain less severe decoupling of DSE relation than shown in Figs. 6(d) to 6(f) because D_R tends to have greater value with shorter δt, and MSAD converges at $\delta t = 100$ fs, which is the longest time interval for integration in our study. Therefore, the interestingly severe decoupling of DSE relation is thus technically quite a reliable result. The physics underneath it, however, is yet to be looked into more deeply.

We believe that diffusion in both translation and rotation occurs with occasional jumps, or excitations. Refs. [1,2] manifested this phenomenon in translational motion of spin models and an atomistic model. Because we can observe the subdiffusive behavior even with the finest time interval, $\delta t = 2$fs, in Fig. S1, we also expect that the angular jumps can be observed in $\Delta\boldsymbol{\phi}$, but rather continuous, not as abrupt as the translational ones.

Concerning the angular jumps, longer time interval, $\delta t \geq 1$ps, would make them to seem abrupt. A proper coarse-graining in time scale could be one way of circumventing this breakdown, but we are not sure if it will be proper or just arbitrary a coarse-graining. We are planning to study on this. Moreover, as we indicated in the main text, because there is no other way, at the present, of calculating angular displacement unboundedly, we adopted this definition for angular displacement.

References

1 Y. Jung, J. P. Garrahan and D. Chandler, *Phys. Rev. E*, 2004, **69**, 061205.

2 D. Jeong, M. Y. Choi, H. J. Kim and Y. Jung, *Phys. Chem. Chem. Phys.*, 2010, **12**, 2001–2010.