Appendix A: The Fourier-Laplace transform of the collective correlation functions

The collective correlation functions in this article are fitted with fit functions. For the sake of simplicity a direct Fourier-Laplace transform of these fit function is desirable instead of the Fourier-Laplace transform of the negative time derivative of these functions. Starting with the collective rotational correlation function $\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_D(t)\Big\rangle$ one may evaluate by means of the product law of integration

$$\begin{aligned}
\mathcal{L}\left[-\frac{d}{dt}\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_D(t)\Big\rangle\right] &= -\int_0^\infty e^{i\omega t}\frac{d}{dt}\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_D(t)\Big\rangle dt \\
&= -\left[\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_D(t)\Big\rangle e^{i\omega t}\right]_0^\infty + i\omega\int_0^\infty e^{i\omega t}\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_D(t)\Big\rangle dt \\
&= \Big\langle \mathbf{M}_D^2\Big\rangle + i\omega\mathcal{L}\left[\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_D(t)\Big\rangle\right] \\
&= \Big\langle \mathbf{M}_D^2\Big\rangle + i\omega\mathcal{L}_{DD}(\omega)
\end{aligned}$$

For the Fourier-Laplace transform of the negative time derivative of cross-correlation function $\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_J(t)\Big\rangle$ one may first calculate the respective $-d/dt\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_J(t)\Big\rangle$:

$$\begin{aligned}
\frac{d}{dt}\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_J(t)\Big\rangle &= \lim_{T\to\infty}\frac{1}{T}\int_0^T \frac{d}{dt}\Big(\mathbf{M}_D(t')\mathbf{M}_J(t+t')\Big)dt' \\
&= \lim_{T\to\infty}\frac{1}{T}\int_0^T \Big(\frac{d\mathbf{M}_D(t')}{dt}\mathbf{M}_J(t+t') + \mathbf{M}_D(t')\frac{d\mathbf{M}_J(t+t')}{dt}\Big)dt' \\
&= \lim_{T\to\infty}\frac{1}{T}\int_0^T \mathbf{M}_D(t')\frac{d\mathbf{M}_J(t+t')}{dt}dt' \\
&= \Big\langle \mathbf{M}_D(0)\cdot\frac{d\mathbf{M}_J(t)}{dt}\Big\rangle \\
&= \Big\langle \mathbf{M}_D(0)\cdot\mathbf{J}(t)\Big\rangle
\end{aligned} \tag{53}$$

This relation is also shown in Fig. 1. The corresponding Fourier-Laplace transform reads

$$\mathcal{L}\left[-\frac{d}{dt}\Big\langle \mathbf{M}_D(0)\cdot\mathbf{M}_J(t)\Big\rangle\right] = \mathcal{L}\left[-\Big\langle \mathbf{M}_D(0)\cdot\mathbf{J}(t)\Big\rangle\right] = -\mathcal{L}_{DJ}(\omega). \tag{54}$$

As mentioned in this article, the computation of $\mathbf{M}_J(t)$ is difficult because of the toroidal jumps of molecules in the simulation box. Therefore, it is desirable to calculate $\mathcal{L}\left[-d/dt\Big\langle \mathbf{M}_J(0)\cdot\mathbf{M}_J(t)\Big\rangle\right]$ in terms of the current autocorrelation function $\Big\langle \mathbf{J}(0)\cdot\mathbf{J}(t)\Big\rangle$. The relation between $\Big\langle \mathbf{M}_J(0)\cdot\mathbf{M}_J(t)\Big\rangle$ and $\Big\langle \mathbf{J}(0)\cdot\mathbf{J}(t)\Big\rangle$ [visualized in Fig. 1] can be easily shown:

$$\frac{d^2}{dt^2}\Big\langle \mathbf{M}_J(0)\cdot\mathbf{M}_J(t)\Big\rangle = \lim_{T\to\infty}\frac{1}{T}\int_0^T \mathbf{M}_J(t')\frac{d^2\mathbf{M}_J(t+t')}{dt^2}dt' \tag{55}$$

$$= \lim_{T\to\infty}\frac{1}{T}\int_0^T \mathbf{M}_J(t')\frac{d^2\mathbf{M}_J(t+t')}{dt'^2}dt' \tag{56}$$

$$= \lim_{T\to\infty}\frac{1}{T}\left[\mathbf{M}_J(t')\frac{d\mathbf{M}_J(t+t')}{dt'}\right]_0^T$$

$$- \lim_{T\to\infty}\frac{1}{T}\int_0^T \frac{d\mathbf{M}_J(t')}{dt'}\frac{\mathbf{M}_J(t+t')}{dt'}dt' \tag{57}$$

$$= -\Big\langle \mathbf{J}(0)\cdot\mathbf{J}(t)\Big\rangle \tag{58}$$

In Eq. (56) we have used:

$$\frac{d\mathbf{M}_J(t+t')}{dt} = \frac{d\mathbf{M}_J(t+t')}{d(t+t')}\cdot\frac{d(t+t')}{dt} \tag{59}$$

$$= \frac{d\mathbf{M}_J(t+t')}{d(t+t')}\cdot\frac{d(t+t')}{dt'} \tag{60}$$

$$= \frac{d\mathbf{M}_J(t+t')}{dt'} \tag{61}$$

since $d(t+t')/dt = d(t+t')/dt' = 1$. The first part of Eq. (57) equals zero since the term in bracket yields finite values for $t' = T$ and $t' = 0$. Taking this into account, the corresponding Fourier-Laplace transform of the time derivative of the collective translational dipole moment is:

$$\mathcal{L}\left[-\frac{d}{dt}\Big\langle \mathbf{M}_J(0)\cdot\mathbf{M}_J(t)\Big\rangle\right] = \int_0^\infty \frac{e^{i\omega t}}{i\omega}\,\frac{d^2}{dt^2}\Big\langle \mathbf{M}_J(0)\cdot\mathbf{M}_J(t)\Big\rangle dt$$

$$- \left[\frac{e^{i\omega t}}{i\omega}\,\frac{d}{dt}\Big\langle \mathbf{M}_J(0)\cdot\mathbf{M}_J(t)\Big\rangle\right]_0^\infty \tag{62}$$

$$= \frac{i}{\omega}\mathcal{L}\left[\Big\langle \mathbf{J}(0)\cdot\mathbf{J}(t)\Big\rangle\right] = \frac{i}{\omega}\mathcal{L}_{JJ}(\omega) \tag{63}$$

The second term in Eq. (62) yields zero since $\Big\langle \mathbf{M}_J(0)\cdot\mathbf{J}(0)\Big\rangle = 0$ and the correlation function $\Big\langle \mathbf{M}_J(0)\cdot\mathbf{M}_J(t)\Big\rangle$ has to relax to zero for infinite time.[27]

Appendix B: The Kohlrausch-William-Watts function

The KWW function

$$f(t) = A \cdot e^{-(t/\tau)^{\beta}} \tag{64}$$

is characterized by three parameters: the amplitude A, the relaxation constant τ and the stretching parameter β. It is often used to represent a superposition of several exponential decays. The corresponding distribution of relaxation times can be computed by:

$$t' \cdot \rho(t') = \frac{-A}{\pi} \sum_{j=0}^{\infty} (-1)^j \frac{\Gamma(\beta j + 1)}{j!} \sin(\pi \beta j) \left(\frac{t'}{\tau}\right)^{\beta j}. \tag{65}$$

with $\Gamma(x) = \int\limits_0^{\infty} t^{x-1} e^{-t} dt$. For special values of $\beta = 1/2, 1/3$ and $2/3$ a closed expression for Eq. (65) exists.[66]

The Fourier-Laplace transform can only be approximated by a series[50,67]

$$\mathcal{L}\left[A \cdot e^{-(t/\tau)^{\beta}}\right] = \frac{-A}{\pi} \sum_{j=0}^{\infty} (-1)^j \frac{\Gamma(\beta j + 1)}{j!} \left(\cos\left(\frac{\pi}{2}\beta j\right) + i \sin\left(\frac{\pi}{2}\beta j\right)\right) \frac{\tau}{(\omega\tau)^{\beta j + 1}} \tag{66}$$

Unfortunately, this series has problems to converge for very low frequencies $\omega \ll \tau^{-1}$. Therefore, one has to switch in this case to the asymptotic series

$$\lim_{\omega\tau \ll 1} \mathcal{L}\left[A \cdot e^{-(t/\tau)^{\beta}}\right] \simeq \frac{A\tau}{\beta} \sum_{j=0}^{\infty} \frac{\Gamma(\frac{j+1}{\beta})}{j!} \left(\cos\left(\frac{\pi}{2} j\right) + i \sin\left(\frac{\pi}{2} j\right)\right) (\omega\tau)^j. \tag{67}$$

In order to avoid the switching between these two series, we represent the dielectric spectrum originating from the KWW function by a Havriliak-Negami function.

Appendix C: Make-up for the residuals

GENDICON offers the possibility to directly calculate the dielectric spectra from the numerical data of the TCFs without the use of fits. Thereby, different time spacing of $\left\langle \mathbf{M}_D(0) \cdot \mathbf{M}_D(t) \right\rangle$,$\left\langle \mathbf{J}(0) \cdot \mathbf{J}(t) \right\rangle$ and $\left\langle \mathbf{M}_D(0) \cdot \mathbf{J}(t) \right\rangle$ cause no problem since the residuals of each TCF is Fourier-Laplace transformed separately. The numerical Fourier-Laplace transform can be used to validate the fit parameters of a given fit or compute contributions which cannot be fitted satisfactorily, e.g. cross-correlation function $\left\langle \mathbf{M}_D(0) \cdot \mathbf{J}(t) \right\rangle$ averaged over a too short time period.

Unfortunately, numerical correlation data may suffer from two problems: First, the time spacing between two points may be to large. This problem occurs when the TCF is evaluated over hundreds of nanoseconds. In order to print or store those functions the time spacing between two data points is often chosen to be several picoseconds. This time spacing is often sufficient to compute the dielectric spectrum up to frequencies of ω <1 THz. Above this frequency the computed spectrum starts to rise to non-physical values. This affects both, the real and the imaginary part. The easiest way to get rid of these numerical Fourier-Laplace transform artefacts is the application of a spline functions.[68,69] The spline does not change significantly the spectrum at lower frequencies [data not shown] but avoids the above mentioned rise at higher frequencies by providing much smaller time steps. GENDICON interpolates the correlation data by a BSPLINE function[70] with selectable time step size.

The second problem of numerical correlation data is the statistical noise which become worse with increasing time. Even if the TCF relaxes more or less to zero, its functional values are not zeros but they oscillate around zero. This fact complicates a direct evaluation by integration of the sinus and cosinus weighted function data. By the way, the computation by FFT methods[71] is difficult since the frequencies ω are usually not equally spaced but distributed on a logarithmic scale. In order to avoid integration problems GENDICON provides two methods: "Trusted time" and the "chirp" function. "Trusted time" means that GENDICON cuts the integration beyond the specified time t. This accelerates the computation of the spectra and neglects the statistical uncertainties of the TCF at long times. Nevertheless, this method does not circumvent the problem of the oscillations around zero. "Chirp" means that GENDICON multiply the original correlation data $f(t)$ with $g(t)$ which is defined by

$$g(t) = \begin{cases} 1 & \text{for} \quad t \leq t_0 \\ e^{-(t-t_0)/\tau_0} & \text{for} \quad t > t_0 \end{cases} \tag{68}$$

This alters the Fourier-Laplace transform in the following way:

$$
\begin{aligned}
\mathcal{L}\left[f(t)\cdot g(t)\right] &= \int\limits_0^\infty f(t)\cdot g(t)e^{i\omega t}dt = \int\limits_0^{t_0} f(t)e^{i\omega t}dt + \int\limits_{t_0}^\infty f(t)\cdot g(t)e^{i\omega t}dt \\
&= \int\limits_0^{t_0} e^{-t/\tau+i\omega t}dt + \int\limits_{t_0}^\infty e^{-t/\tau-(t-t_0)/\tau_0+i\omega t}dt \\
&= \left[\frac{e^{-t/\tau+i\omega t}}{-1/\tau+i\omega}\right]_0^{t_0} + \left[\frac{e^{-t/\tau-(t-t_0)/\tau_0+i\omega t}}{-1/\tau-1/\tau_0+i\omega}\right]_{t_0}^\infty
\end{aligned} \tag{69}
$$

In a multi-exponential fit it is the longest relaxation time τ which is relevant for chirp procedure. Therefore, it is sufficient to demonstrate its action on a single exponential τ. If $t_0 \gg \tau$ the first term on the right hand side of Eq. (69) equals the Fourier-Laplace transform of the exponential function since the upper integration limit does not contribute significantly to the result. The same arguments make the second term on the right hand side negligible. In other words, the character of the Fourier-Laplace transform of an exponential is not altered by the “chirp” function if a $t_0 \gg \tau$ is chosen. If t_0 is not much bigger than τ one has to increase τ_0 to make $1/\tau_0$ very small. In this case, the upper limit of the first term and the lower limit of the second term on the right hand side of Eq. (69) cancel.