

# Dielectric spectra of ionic liquids and their conversion to solvation dynamics: a detailed computational analysis of polarizable systems†

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Michael Schmollngruber, Christian Schröder\* and Othmar Steinhauser

For the three molecular ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-butyl-3-methylimidazolium tetrafluoroborate, dielectric spectra were calculated from molecular dynamics simulations based on polarizable force fields. Using the reaction field continuum model the dielectric spectra were converted to the solvation dynamics of coumarin 153. It is shown in detail that the inclusion of the static conductivity in this model is essential. When simplifying the dielectric spectrum to the static conductivity hyperbola, the solvation response function becomes mono-exponential. Taking into account the frequency dependence of the conductivity, the typical two time-regimes of the solvation response function in ionic liquids are already obtained. However, the mean relaxation time remains the same. When converting the complete dielectric spectrum, *i.e.* also including frequency-dependent dielectric permittivity, quantitative changes are observed, but the qualitative shape is conserved. In accordance with previous experimental studies, solvation dynamics in ionic liquids predicted by the reaction field continuum model is too fast for longer times. This correlates with the suppression of the fine structure of the dielectric spectrum at low frequencies by the static conductivity hyperbola. By scaling down the static conductivity this effect can be partially amended. In addition to the impact of the solvent dielectric spectrum on solvation dynamics, solute-specific effects, *i.e.* anisotropy in shape and charge distribution as well as polarizability, were also studied.

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## 1. Introduction

Ionic liquids are characterized by an anisotropy in charge distribution and shape. This combination makes them a challenging class of soft matter when dealing with their electrostatic or dielectric properties, as they unite the properties of polar liquids and ionic melts. At the molecular level, they have a net charge and a dipole moment and as opposed to ionic solutions, both reside on the very same molecule. At the dielectric or at the mesoscopic level these properties correspond to the dielectric conductivity  $\mathcal{J}(\omega)$  and the dielectric permittivity  $\epsilon(\omega)$ , respectively.<sup>1–3</sup> While the former stands for collective translation, the latter is representative of collective rotation. In any case, it is the response to an applied external electric field, as measured in dielectric spectroscopy. An alternative method is to detect the internal Maxwell field exerted on a solute used as a probe, being Coumarin 153 in most cases.<sup>4–10</sup> In this case, the solute is excited to its electronic  $S_1$  state and it is the

accompanying change in the dipole moment that is coupling to the Maxwell field. The relaxation of the surrounding solvent after the excitation of the solute is recorded *via* time-resolved fluorescence spectroscopy, yielding what is commonly known as the solvation response function or solvation dynamics. This method has a long tradition for polar solvents.<sup>11–17</sup> In recent years, it was also applied to ionic liquids.<sup>5–9,18–34</sup>

As both methods, dielectric spectroscopy and solvation dynamics, operate using electric fields, either as a perturbation or as a response, investigations into their mutual relation exist in the literature. In most of these studies the focus was on experimental data.<sup>6–9,21,32,35</sup> In this study we operate using computational methods, calculating the dielectric spectrum and the solvation response function from the very same simulation. For the conversion of the former into the latter we use the reaction field continuum model (RFCM), because it does not need data from a source other than the dielectric spectrum. In previous studies based on experimental dielectric spectra, the RFCM worked very well for polar liquids, but faced problems for charged dipolar systems, *i.e.* ionic liquids. A computational approach allows us to study how parts of the dielectric spectrum – when considered separately – influence the solvation response function. In this way we hope to elucidate the peculiar

Department of Computational Biological Chemistry, University of Vienna,  
Währingerstrasse 17, A-1090 Vienna, Austria.  
E-mail: [christian.schroeder@univie.ac.at](mailto:christian.schroeder@univie.ac.at)

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problems encountered<sup>6–9,32</sup> when applying the RFCM to ionic liquids.

Recently, there have also been other attempts beyond those based on a simple continuum model to predict the solvation response function of ionic liquids, either employing a semi-molecular approach<sup>30,31</sup> or an extended Debye–Hückel model.<sup>5</sup>

This paper is organized as follows: in the theory section a short overview of the development of the RFCM and its application to ionic liquids is given. Special attention was paid to anisotropic features of the solute C153. The Results and discussion section starts with the presentation of the computational dielectric spectra. Subsequently, the solvation response function is characterized within the framework of the RFCM. Fundamental analytic results are collected in the appendix and background information concerning the calculation of the dielectric spectra is given in the ESI.†

## II. Theory

### A. Calculation of the solvation response function from the frequency-dependent generalized dielectric constant

The normalized time-dependent solvation response function is given by

$$S(t) = \frac{\Delta U(t) - \Delta U(\infty)}{\Delta U(0) - \Delta U(\infty)}, \quad (1)$$

where  $U(t)$  is the solvation energy. At time  $t = 0$  the charge distribution of a chromophore molecule embedded in a solvent is changed due to photoexcitation. The relaxation of the solvent molecules in response to this change in the charge distribution  $\Delta\rho(\vec{r}, t)$  of the solute results in a transient shift of the solvation energy,

$$\Delta U(t) = \frac{1}{2} \int \Delta\rho(\vec{r}, t) \Phi(\vec{r}, t) d\vec{r}, \quad (2)$$

where  $\Phi(\vec{r}, t)$  is the total electrostatic potential exerted by the solvent. A first approximation of this potential is given by enclosing the charge distribution of the solute  $\Delta\rho(\vec{r}, t)$  in a spherical cavity of radius  $a$  and describing the solvent outside by a dielectric continuum with a static dielectric constant  $\epsilon$ :

$$\Phi(\vec{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} -\frac{\epsilon - \epsilon_c}{\epsilon + \epsilon_c} \frac{q_m^l}{a^{2l+1}} r^l Y_m^l(\theta, \phi). \quad (3)$$

Furthermore, it is assumed that the cavity is filled with a dielectric medium characterized by the constant  $\epsilon_c$ . The spatial variation of the potential within the cavity is described by the solid spherical harmonics  $r^l Y_m^l(\theta, \phi)$ . The anisotropy of the charge distribution of the solute is characterized by its multipole moments,

$$q_m^l = \int \Delta\rho(\vec{r}) r^l Y_m^l(\theta, \phi) d\vec{r}. \quad (4)$$

Inserting the static potential  $\Phi(\vec{r})$  into eqn (2) one gets the temporal average of the solvation energy,

$$\langle \Delta U \rangle = -\frac{1}{2} \sum_{l=0}^{\infty} \frac{\epsilon - \epsilon_c}{\epsilon + \epsilon_c} \frac{1}{a^{2l+1}} \sum_{m=-l}^{+l} q_m^l q_m^{l*}. \quad (5)$$

For the special case  $l = 1$ , *i.e.* for a single dipole  $\vec{\mu}$  enclosed in the cavity this reduces to the original formula of Böttcher and Bordewijk:<sup>36</sup>

$$\langle \Delta U_{\mu} \rangle = -\frac{1}{2} \frac{\Delta\vec{\mu}^2}{a^3} \frac{\epsilon - \epsilon_c}{\epsilon + \epsilon_c} = -\frac{1}{2} \Delta\vec{\mu} \cdot \vec{E}_{\text{RF}}, \quad (6)$$

where in the second step we have introduced the reaction field

$$\vec{E}_{\text{RF}} = \frac{\Delta\vec{\mu} \epsilon - \epsilon_c}{a^3 \epsilon + \frac{\epsilon_c}{2}}. \quad (7)$$

The factor  $\Delta\vec{\mu}^2/a^3$  in eqn (6) is a dipolar energy representative of the solute. The dimensionless co-factor involving the dielectric constant stands for the solvation properties of the solvent. Maroncelli and Fleming<sup>37</sup> realized that eqn (7) gives an incorrect limit for  $\epsilon = 1$ , *i.e.* the reaction field does not vanish in the absence of a solvent, but gives a value dependent on  $\epsilon_c$ . In fact, this represents a spurious self-interaction of the solute dipole with its own cavity. This can be amended using the method of Mazurenko<sup>38</sup> as recommended by Maroncelli and Fleming.<sup>37</sup> This method augments the permanent dipole moment  $\Delta\vec{\mu}$  by an induced contribution  $\Delta\vec{\mu}_{\text{ind}} = \alpha \vec{E}_{\text{RF}}$

$$\vec{E}_{\text{RF}} = \frac{\Delta\vec{\mu} + \alpha \vec{E}_{\text{RF}} \epsilon - 1}{a^3 \epsilon + \frac{1}{2}}, \quad (8)$$

where  $\alpha$  is the molecular polarizability of the solute. Consequently,  $\epsilon_c$  was set to unity. However, it re-enters *via* the Clausius–Mosotti equation

$$\frac{\alpha}{a^3} = \frac{\epsilon_c - 1}{\epsilon_c + 2}, \quad (9)$$

yielding

$$\vec{E}_{\text{RF}} = \frac{\Delta\vec{\mu} \epsilon_c + 2 \epsilon - 1}{a^3 \frac{3}{\epsilon + \frac{\epsilon_c}{2}}}. \quad (10)$$

So far, the reaction field is only a temporal average as it includes only the static dielectric constant. To introduce the time dependence we start from the constitutive relation in the frequency domain

$$\vec{P}(\vec{r}, \omega) = \frac{\epsilon(\omega) - 1}{4\pi} \vec{E}(\vec{r}, \omega), \quad (11)$$

giving the dielectric polarization  $\vec{P}(\vec{r}, \omega)$  for systems composed of neutral dipolar molecules. Both,  $\vec{P}(\vec{r}, \omega)$  and  $\vec{E}(\vec{r}, \omega)$  can be combined to the dielectric displacement

$$\vec{D}(\vec{r}, \omega) = \vec{E}(\vec{r}, \omega) + 4\pi \vec{P}(\vec{r}, \omega) = \epsilon(\omega) \vec{E}(\vec{r}, \omega). \quad (12)$$

The static reaction field (eqn (7)) was obtained as a solution of the Laplace equation under the boundary conditions that the parallel component of  $\vec{E}(\vec{r})$  and the normal component of  $\vec{D}(\vec{r})$  are continuous at the spherical surface. Again applying these boundary

conditions, but now to the general frequency-dependent electric field and dielectric displacement (eqn (12)), yields<sup>39</sup>

$$\vec{E}_{\text{RF}}(\omega) = \frac{\Delta\vec{\mu}\varepsilon_c + 2}{a^3} \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + \frac{\varepsilon_c}{2}} \quad (13)$$

Here,  $\varepsilon_c$  as a constant value describes the fixed geometry of the solute, whereas  $\varepsilon(\omega)$  stands for the relaxation of the solvent. As an ionic liquid is composed of charged, dipolar molecules, its dielectric properties have to be described by the generalized permittivity,<sup>3</sup>

$$\Sigma(\omega) = \varepsilon(\omega) - 1 + \frac{4\pi i\sigma(\omega)}{\omega}, \quad (14)$$

where the dielectric conductivity  $4\pi i\sigma(\omega)/\omega$  describes the creation of collective dipole moments by the mutual translational motion of charged species. This generalizes the constitutive relation to

$$\vec{P}(\vec{r}, \omega) = \frac{\Sigma(\omega)}{4\pi} \vec{E}(\vec{r}, \omega) \quad (15)$$

and the dielectric displacement to

$$\vec{D}(\vec{r}, \omega) = \vec{E}(\vec{r}, \omega) + 4\pi\vec{P}(\vec{r}, \omega) = (\Sigma(\omega) + 1)\vec{E}(\vec{r}, \omega). \quad (16)$$

In other words, for charged dipolar systems,  $\Sigma(\omega) + 1$  replaces  $\varepsilon(\omega)$  in eqn (12) in the case of neutral dipolar systems. Applying the same boundary conditions as above the reaction field can be generalized to

$$\vec{E}_{\text{RF}}(\omega) = \frac{\Delta\vec{\mu}\varepsilon_c + 2}{a^3} \frac{\Sigma(\omega)}{\Sigma(\omega) + 1 + \frac{\varepsilon_c}{2}} \quad (17)$$

Generalizing the theory developed by Hsu *et al.*<sup>39</sup> for neutral dipolar solvents to the case of ionic liquids by replacing eqn (13) with eqn (17) we get the analogous expression for the solvation energy

$$\Delta U_{\Sigma}(t) = \frac{2}{\pi} \int_0^{\infty} \frac{\cos(\omega t)}{\omega} \text{Im} \left[ \frac{\Sigma(\omega)}{\Sigma(\omega) + 1 + \frac{\varepsilon_c}{2}} \right] d\omega. \quad (18)$$

Strictly speaking, the above equation should contain the dipolar energy  $-(\Delta\vec{\mu}^2/a^3)((\varepsilon_c + 2)/3)$  as a prefactor. However, when substituting  $\Delta U(t)$  into eqn (1), giving the solvation response function, the dipolar energy cancels out. Therefore, it is omitted in the above and following equations, where only the dimensionless part is retained.

## B. Analytical calculation of the mean relaxation time of $S_{\Sigma}(t)$

At the global level, the most important property of the solvation response function  $S_{\Sigma}(t)$  is its mean relaxation time

$$\tau_{\Sigma} = \int_0^{\infty} S_{\Sigma}(t) dt. \quad (19)$$

According to eqn (1),  $S_{\Sigma}(t)$  is calculated from the solvation energy  $\Delta U_{\Sigma}$  at times  $t$ , zero and infinity. As the asymptotic value

of  $\Delta U_{\Sigma}(t)$  approaches values close to zero (data not shown), its asymptotic value is omitted in order to simplify  $S_{\Sigma}(t)$  to

$$S_{\Sigma}(t) \simeq \frac{\Delta U_{\Sigma}(t)}{\Delta U_{\Sigma}(0)}. \quad (20)$$

Consequently, the mean relaxation time is given by

$$\tau_{\Sigma} = \frac{T}{\Delta U_{\Sigma}(0)}, \quad (21)$$

where

$$T = \int_0^{\infty} \Delta U_{\Sigma}(t) dt \quad (22)$$

$$= \lim_{\omega \rightarrow 0} \frac{1}{\omega} \text{Im} \left[ \frac{\Sigma(\omega)}{\Sigma(\omega) + 1 + \frac{\varepsilon_c}{2}} \right] \quad (23)$$

$$= \lim_{\omega \rightarrow 0} \frac{1}{\omega} \frac{\left(1 + \frac{\varepsilon_c}{2}\right) \Sigma''(\omega)}{\left(\Sigma'(\omega) + 1 + \frac{\varepsilon_c}{2}\right)^2 + (\Sigma''(\omega))^2}. \quad (24)$$

With

$$\Sigma(\omega) = \varepsilon(\omega) - 1 + \frac{4\pi i\sigma(\omega)}{\omega} \quad (25)$$

$$\Sigma(\omega) = \Sigma'(\omega) + i\Sigma''(\omega) \quad (26)$$

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \quad (27)$$

$$\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega). \quad (28)$$

Eqn (24) can be rewritten upon substitution as

$$T = \lim_{\omega \rightarrow 0} \frac{1}{\omega} \text{Im} \left[ \frac{\Sigma(\omega)}{\Sigma(\omega) + 1 + \frac{\varepsilon_c}{2}} \right] \quad (29)$$

$$= \lim_{\omega \rightarrow 0} \frac{\left(1 + \frac{\varepsilon_c}{2}\right) (\varepsilon''(\omega)\omega + 4\pi\sigma'(\omega))}{\left(\omega \left(\varepsilon'(\omega) + \frac{\varepsilon_c}{2}\right) - 4\pi\sigma''(\omega)\right)^2 + (\omega\varepsilon''(\omega) + 4\pi\sigma'(\omega))^2} \quad (30)$$

$$= \lim_{\omega \rightarrow 0} \frac{\left(1 + \frac{\varepsilon_c}{2}\right) 4\pi\sigma'(\omega)}{(-4\pi\sigma''(\omega))^2 + (4\pi\sigma'(\omega))^2} \quad (31)$$

$$= \lim_{\omega \rightarrow 0} \left(1 + \frac{\varepsilon_c}{2}\right) \frac{1}{4\pi\sigma'(\omega)} \quad (32)$$

$$= \left(1 + \frac{\varepsilon_c}{2}\right) \frac{1}{4\pi\sigma_0}. \quad (33)$$

When proceeding from eqn (30) to (31) we have omitted all terms involving  $\varepsilon'(\omega)$  and  $\varepsilon''(\omega)$  as they are multiplied by  $\omega$  and thus vanish in the zero-frequency limit. Furthermore,  $\lim_{\omega \rightarrow 0} \sigma''(\omega) = 0$ .

As can be seen from eqn (21), the calculation of the mean relaxation time needs both the time integral (see eqn (22)) and

the amplitude  $\Delta U_{\Sigma}(0)$ . For  $t = 0$ , eqn (18) becomes

$$\Delta U_{\Sigma}(0) = \frac{2}{\pi} \int_0^{\infty} \frac{1}{\omega} \operatorname{Im} \left[ \frac{\Sigma(\omega)}{\Sigma(\omega) + 1 + \frac{\varepsilon_c}{2}} \right] d\omega. \quad (34)$$

Following the elegant formalism described by Rips *et al.*,<sup>40</sup> we get

$$\Delta U_{\Sigma}(0) = \lim_{\omega \rightarrow 0} \left[ \frac{\Sigma(\omega)}{\Sigma(\omega) + 1 + \frac{\varepsilon_c}{2}} \right] - \lim_{\omega \rightarrow \infty} \left[ \frac{\Sigma(\omega)}{\Sigma(\omega) + 1 + \frac{\varepsilon_c}{2}} \right] \quad (35)$$

Using eqn (25)–(28), the infinite-frequency limit above gives

$$\lim_{\omega \rightarrow \infty} \left[ \frac{\Sigma(\omega)}{\Sigma(\omega) + 1 + \frac{\varepsilon_c}{2}} \right] = \frac{2(\varepsilon_{\infty} - 1)}{2(\varepsilon_{\infty} - 1) + \varepsilon_c + 2}, \quad (36)$$

while the zero-frequency limit gives unity. Altogether, the amplitude becomes

$$\Delta U_{\Sigma}(0) = \frac{\varepsilon_c + 2}{\varepsilon_c + 2\varepsilon_{\infty}}. \quad (37)$$

Combining eqn (33) and (37) we get the mean relaxation time

$$\tau_{\Sigma} = \frac{T}{\Delta U_{\Sigma}(0)} = \frac{\varepsilon_c + 2\varepsilon_{\infty}}{2} \frac{1}{4\pi\sigma_0}. \quad (38)$$

This shows that  $\tau_{\Sigma}$  is determined by only three parameters, namely  $\varepsilon_c$ ,  $\sigma_0$  and  $\varepsilon_{\infty}$ .  $\varepsilon_c$  characterizes the polarizability of the solute,  $\sigma_0$  stands for the translational mobility of the solvent environment and  $\varepsilon_{\infty}$  describes the polarizability of the solvent. Although the above derivation differs in parts, we get the same analytical results for the mean relaxation time as Zhang *et al.*<sup>6</sup>

### C. Using the components of the dielectric spectrum to calculate the solvation response function

While experiments always yield the dielectric spectrum as an inseparable entity, except for the static conductivity  $\sigma_0$ , which is also accessible from other experimental methods, simulation studies offer the possibility of analyzing how different components of the computational spectrum determine the shape of the solvation response function  $S(t)$ . For conducting systems, the hyperbola  $4\pi i\sigma_0/\omega$  dominates the imaginary part of the generalized dielectric permittivity  $\Sigma(\omega)$ . Therefore, it is usually subtracted:

$$\Sigma_0(\omega) = \Sigma(\omega) - \frac{4\pi i\sigma_0}{\omega} = \varepsilon(\omega) - 1 + \frac{4\pi i(\sigma(\omega) - \sigma_0)}{\omega}. \quad (39)$$

The complement  $\Sigma_0(\omega)$  of the conductivity hyperbola  $4\pi i\sigma_0/\omega$  is representative of the fine structure of the spectrum. Its role can be highlighted by reducing eqn (18) to

$$\Delta U_{\Sigma_0}(t) = \frac{2}{\pi} \int_0^{\infty} \frac{\cos(\omega t)}{\omega} \operatorname{Im} \left[ \frac{\Sigma_0(\omega)}{\Sigma_0(\omega) + 1 + \frac{\varepsilon_c}{2}} \right] d\omega. \quad (40)$$

The subtraction of  $4\pi i\sigma_0/\omega$  corresponds to the replacement of  $\sigma'(\omega)$  with  $(\sigma'(\omega) - \sigma_0)$  in eqn (32):

$$\int_0^{\infty} \Delta U_{\Sigma_0}(t) dt = \lim_{\omega \rightarrow 0} \left( 1 + \frac{\varepsilon_c}{2} \right) \frac{1}{4\pi(\sigma'(\omega) - \sigma_0)}. \quad (41)$$

Unfortunately, this integral diverges. In other words, the inclusion of the conductivity hyperbola is essential for this model theory.<sup>7</sup> Because of its fundamental role, it makes sense to study the influence of  $4\pi i\sigma_0/\omega$  separately, simplifying eqn (18) to

$$\Delta U_{\sigma_0}(t) = \frac{2}{\pi} \int_0^{\infty} \frac{\cos(\omega t)}{\omega} \operatorname{Im} \left[ \frac{\frac{4\pi i\sigma_0}{\omega}}{\frac{4\pi i\sigma_0}{\omega} + 1 + \frac{\varepsilon_c}{2}} \right] d\omega \quad (42)$$

$$= \frac{2}{\pi} \int_0^{\infty} \cos(\omega t) \frac{T}{1 + (\omega T)^2} d\omega \quad (43)$$

$$= e^{-t/T} \quad (44)$$

with the relaxation time

$$T = \left( 1 + \frac{\varepsilon_c}{2} \right) \frac{1}{4\pi\sigma_0}. \quad (45)$$

In other words, the conductivity hyperbola – when taken solely – leads to a mono-exponential function. To get a more realistic  $S(t)$ , the logical next step is to replace the static conductivity  $\sigma_0$  by its frequency-dependent analogue  $\sigma(\omega)$ , yielding

$$\Delta U_{\sigma}(t) = \frac{2}{\pi} \int_0^{\infty} \frac{\cos(\omega t)}{\omega} \operatorname{Im} \left[ \frac{\frac{4\pi i\sigma(\omega)}{\omega}}{\frac{4\pi i\sigma(\omega)}{\omega} + 1 + \frac{\varepsilon_c}{2}} \right] d\omega, \quad (46)$$

which represents the complete translational contribution. Referring to eqn (31) it is clear that this replacement does not affect  $T$ . Thus we have shown that  $T$  is universal for all three cases discussed. The amplitudes, however, differ. Repeating the calculation in eqn (35) for  $4\pi i\sigma_0/\omega$  or  $4\pi i\sigma(\omega)/\omega$  instead of  $\Sigma(\omega)$  we get  $\Delta U_{\sigma_0}(0) = \Delta U_{\sigma}(0) = 1$ . Hence, the mean relaxation time for these two cases is  $\tau_{\sigma_0} = \tau_{\sigma} = T$  as opposed to eqn (38). We anticipate from the results shown later that time dependence of  $S_{\sigma_0}(t)$  and  $S_{\sigma}(t)$  is rather different, although the respective mean relaxation times are identical.

### D. Describing the solute using an ellipsoidal cavity

All previous expressions are based on a spherical cavity containing the solute. As the studied solute coumarin 153 is rather anisotropic in shape it seems prudent to make the cavity anisotropic as well. Following previous reports using reaction field methods with an ellipsoidal solute cavity in polar liquids,<sup>39,41–43</sup> we applied this approach to ionic liquids. The response function in this case is given by

$$F(\omega) = \begin{pmatrix} f_a(\omega) & 0 & 0 \\ 0 & f_b(\omega) & 0 \\ 0 & 0 & f_c(\omega) \end{pmatrix}, \quad (47)$$

where

$$f_i = \frac{3A_i(1 - A_i)\Sigma(\omega)}{1 + \Sigma(\omega)(1 - A_i)}, \quad i = a, b, c \quad (48)$$

describe the response function along the three axes of the ellipsoid and  $A_i$  are ellipsoidal shape factor integrals.<sup>41</sup> The solvation energy is then given by

$$\Delta U(t) = -\frac{\epsilon_c + 2}{3abc} \Delta\mu \cdot \frac{2}{\pi} \int_0^\infty \frac{\cos(\omega t)}{\omega} \text{Im}[F(\omega)] d\omega \cdot \Delta\mu. \quad (49)$$

### III. Methods

The results presented here were gathered from polarizable molecular dynamics simulations of three different ionic liquids, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup>), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM<sup>+</sup>TfO<sup>−</sup>) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup>), each containing 1000 ion pairs and a single coumarin 153 (C153) molecule with a charge distribution reflecting its electronic ground state. All simulations were run at a temperature of 300 K in cubic boxes with respective box lengths of 64.4 Å for EMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup>, 67.9 Å for EMIM<sup>+</sup>TfO<sup>−</sup> and 68.65 Å for BMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup> using a time step of 0.5 fs. Non-bonded interactions were calculated using the Lennard-Jones potential with a switch function between 11 and 12 Å and the PME method<sup>44,45</sup> with a real-space cut-off of 12 Å and a  $\kappa$  of 0.41 Å<sup>−1</sup>. The lengths of all bonds involving a hydrogen atom were held fixed by the SHAKE algorithm.<sup>46</sup> The charge distribution of the solvent molecules was made polarizable by adding Drude particles to all non-hydrogen atoms.<sup>47</sup> These simulations are the same as in ref. 10, where more detailed information about the computational setup is given. For each system, 60 ns of trajectory data containing only coordinates and additional 15 ns of trajectory data also containing velocities were produced using the molecular dynamics package CHARMM.<sup>48</sup> For a quantification of the various solvation response functions we fitted them to the function

$$S(t) \approx ae^{-t/\tau_1} + (1 - a)e^{-(t/\tau_2)\beta}, \quad (50)$$

consisting of an exponential and a Kohlrausch–William–Watts (KWW) function.<sup>10,12,25,35</sup> The set of parameters is collected in Table 1.

## IV. Results and discussion

### A. Dielectric spectra

The dielectric relaxation data shown in Fig. 1 were calculated from molecular dynamics simulation data following the approach used in the previous work.<sup>3</sup> The time correlation functions of the total rotational dipole moment ( $\langle \vec{M}_D(0) \cdot \vec{M}_D(t) \rangle$ ), the total current ( $\langle \vec{J}(0) \cdot \vec{J}(t) \rangle$ ) and their cross-correlation function ( $\langle \vec{M}_D(0) \cdot \vec{J}(t) \rangle$ ) were fitted using fit functions of the form

$$f(t) \approx \sum_j A_j \cdot e^{-t/\tau_j} + \sum_k A_k \cos(\omega_k t + \delta_k) \cdot e^{-t/\tau_k}, \quad (51)$$

where  $f(t)$  denotes the respective time correlation function. In order to achieve a more reliable value for the longest time

**Table 1** A list of all fit parameters used to describe the different variants of  $S_X(t)$ ,  $S_{\text{exp}}(t)$  and  $C(t)$ . The value of  $\epsilon_c$  describes the polarizability of C153 within the RFCM (see eqn (9)).  $\sigma_0^{\text{eff}} = \sigma_0/2.4$  denotes an effective, empirically determined<sup>6,9,32</sup> static conductivity. Graphical representations of the functions listed here can be found in Fig. 2, 4 and 6

		$\epsilon_c$	$\sigma_0/\sigma_0^{\text{eff}}$	$a$	$\tau_1/\text{ps}$	$\tau_2/\text{ps}$	$\beta$	$\tau_X/\text{ps}$
EMIM <sup>+</sup> BF <sub>4</sub> <sup>−</sup>	$S_{\sigma_0}(t)$	1	$\sigma_0$	1.0	2.63	—	—	2.63
	$S_{\sigma}(t)$	1	$\sigma_0$	0.55	0.138	3.41	0.58	2.63
	$S_{\Sigma}(t)$	1	$\sigma_0$	0.42	0.189	4.27	0.58	4.08
	$S_{\Sigma}(t)$	2	$\sigma_0$	0.37	0.209	4.95	0.60	4.95
	$S_{\Sigma}(t)$	3	$\sigma_0$	0.33	0.225	5.69	0.61	5.83
	$S_{\Sigma}(t)$	1	$\sigma_0^{\text{eff}}$	0.45	0.206	9.88	0.54	9.75
	$S_{\Sigma}(t)$	2	$\sigma_0^{\text{eff}}$	0.40	0.232	11.8	0.55	11.8
	$S_{\Sigma}(t)$	3	$\sigma_0^{\text{eff}}$	0.37	0.256	13.8	0.57	13.9
	$C(t)^{10}$	—	—	0.45	0.238	217	0.40	397
	$S_{\text{exp}}(t)^7$	—	—	0.55	0.269	87.2	0.52	73.3
	$S_{\text{ell}}(t)$	1	$\sigma_0$	0.46	0.177	3.94	0.58	3.58
	$S_{\text{ell}}^a(t)$	1	$\sigma_0$	0.46	0.176	3.93	0.58	3.58
	$S_{\text{ell}}^b(t)$	1	$\sigma_0$	0.43	0.186	4.19	0.58	3.95
	$S_{\text{ell}}^c(t)$	1	$\sigma_0$	0.36	0.212	5.08	0.60	5.11
EMIM <sup>+</sup> TfO <sup>−</sup>	$S_{\sigma_0}(t)$	1	$\sigma_0$	1.0	3.79	—	—	3.79
	$S_{\sigma}(t)$	1	$\sigma_0$	0.50	0.147	4.53	0.58	3.79
	$S_{\Sigma}(t)$	1	$\sigma_0$	0.48	0.169	5.81	0.50	6.18
	$S_{\Sigma}(t)$	2	$\sigma_0$	0.43	0.187	6.59	0.51	7.44
	$S_{\Sigma}(t)$	3	$\sigma_0$	0.39	0.201	7.48	0.52	8.70
	$S_{\Sigma}(t)$	1	$\sigma_0^{\text{eff}}$	0.55	0.193	15.7	0.48	14.7
	$S_{\Sigma}(t)$	2	$\sigma_0^{\text{eff}}$	0.51	0.223	18.7	0.50	17.7
	$S_{\Sigma}(t)$	3	$\sigma_0^{\text{eff}}$	0.48	0.252	21.8	0.51	20.7
	$C(t)^{10}$	—	—	0.32	0.285	227	0.37	646
	$S_{\text{exp}}(t)^7$	—	—	0.45	0.233	277	0.49	317
	$S_{\text{ell}}(t)$	1	$\sigma_0$	0.52	0.158	5.44	0.49	5.48
	$S_{\text{ell}}^a(t)$	1	$\sigma_0$	0.52	0.158	5.43	0.49	5.46
	$S_{\text{ell}}^b(t)$	1	$\sigma_0$	0.49	0.167	5.71	0.50	6.00
	$S_{\text{ell}}^c(t)$	1	$\sigma_0$	0.42	0.189	6.74	0.51	7.67
BMIM <sup>+</sup> BF <sub>4</sub> <sup>−</sup>	$S_{\sigma_0}(t)$	1	$\sigma_0$	1.0	15.2	—	—	15.2
	$S_{\sigma}(t)$	1	$\sigma_0$	0.58	0.161	27.6	0.68	15.2
	$S_{\Sigma}(t)$	1	$\sigma_0$	0.53	0.196	38.5	0.70	23.2
	$S_{\Sigma}(t)$	2	$\sigma_0$	0.48	0.222	43.7	0.72	28.2
	$S_{\Sigma}(t)$	3	$\sigma_0$	0.44	0.245	48.9	0.73	33.2
	$S_{\Sigma}(t)$	1	$\sigma_0^{\text{eff}}$	0.56	0.233	99.7	0.71	52.6
	$S_{\Sigma}(t)$	2	$\sigma_0^{\text{eff}}$	0.52	0.275	113	0.73	63.5
	$S_{\Sigma}(t)$	3	$\sigma_0^{\text{eff}}$	0.49	0.319	127	0.76	74.0
	$C(t)^{10}$	—	—	0.40	0.245	1260	0.31	6070
	$S_{\text{exp}}(t)^7$	—	—	0.38	0.266	202	0.52	233.7
	$S_{\text{ell}}(t)$	1	$\sigma_0$	0.56	0.181	35.7	0.69	20.4
	$S_{\text{ell}}^a(t)$	1	$\sigma_0$	0.56	0.181	35.6	0.69	20.3
	$S_{\text{ell}}^b(t)$	1	$\sigma_0$	0.53	0.192	37.8	0.70	22.5
	$S_{\text{ell}}^c(t)$	1	$\sigma_0$	0.47	0.226	44.7	0.72	29.1

constant of  $\langle \vec{J}(0) \cdot \vec{J}(t) \rangle$ ,<sup>3</sup> the relationship

$$\frac{d^2}{dt^2} \left\langle \left( \Delta \vec{M}_J(t) \right)^2 \right\rangle = 2 \left\langle \vec{J}(0) \cdot \vec{J}(t) \right\rangle \quad (52)$$

described in ref. 49 was practically applied. As  $\langle (\Delta \vec{M}_J(t))^2 \rangle$  could be calculated from the much longer coordinate trajectory,  $\langle \vec{J}(0) \cdot \vec{J}(t) \rangle$  gained by calculating the second derivative using the Savitzky–Golay algorithm<sup>50</sup> proved to be consistent with the directly calculated correlation function (cf. Fig. S1 provided in the ESI<sup>†</sup>). This provided another source for the above-mentioned



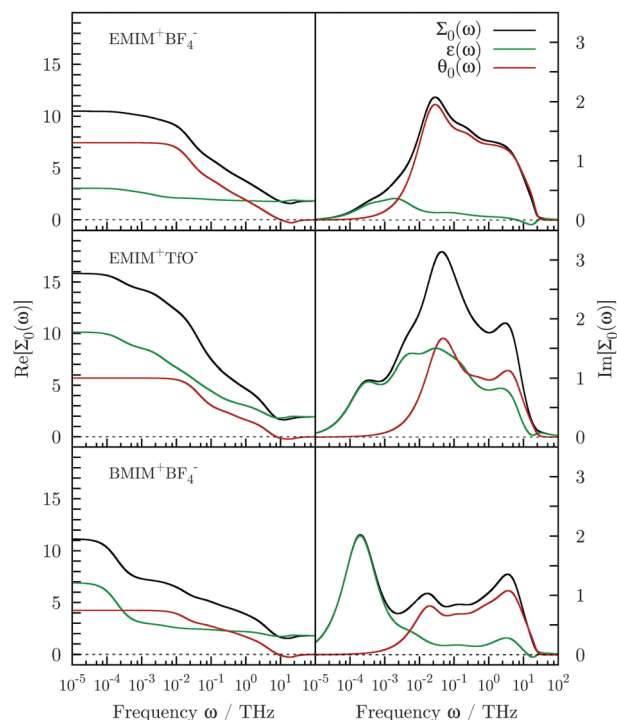


Fig. 1 Dielectric relaxation functions (cf. eqn (39)) generated from MD simulation data, real (left column) and imaginary parts (right column).

longest time constant. Tables S1–S3 in the ESI† list all the fit parameters used here.

## B. Characterization of the solvation response function within the reaction field continuum model

**1. The time dependence.** As we have already learned in eqn (41), the static conductivity  $\sigma_0$  is of central importance when applying the reaction field continuum model (RFCM) to conducting systems. Therefore, we study its properties first. The values calculated for the three systems studied here are  $0.402 \text{ S m}^{-1}$ ,  $0.279 \text{ S m}^{-1}$  and  $0.069 \text{ S m}^{-1}$  for  $\text{EMIM}^+\text{BF}_4^-$ ,  $\text{EMIM}^+\text{TfO}^-$  and  $\text{BMIM}^+\text{BF}_4^-$ , respectively.  $S_{\sigma_0}(t)$  is a mono-exponential function (see eqn (44) and Fig. 2). This, however, does not reflect the typical two time regimes of the solvation response function in ionic liquids.

The next logical step is the full frequency-dependent conductivity  $\sigma(\omega)$ . In fact, this extension already generates two time regimes in the solvation response function, as can be seen in Fig. 2 and Table 1. When compared to the mono-exponential function typical for the static conductivity,  $S_{\sigma_0}(t)$  already has a shape that can be modeled by the fit function (50). As the actual amplitudes derived from the fit are almost equal, we are facing a one-to-one mixture of an exponential and a KWW function.

With the above description, the essentials of translational motion are represented within the RFCM. In order to include rotational motion, we replace  $4\pi i\sigma(\omega)/\omega$  by  $\Sigma(\omega)$  and use eqn (18). This changes  $S(t)$  quantitatively, but not qualitatively, as can be seen in Fig. 2 and Table 1. The inclusion of  $\varepsilon(\omega) - 1$ , i.e. the change from  $S_{\sigma_0}(t)$  to  $S_{\Sigma}(t)$ , changes the fit parameters

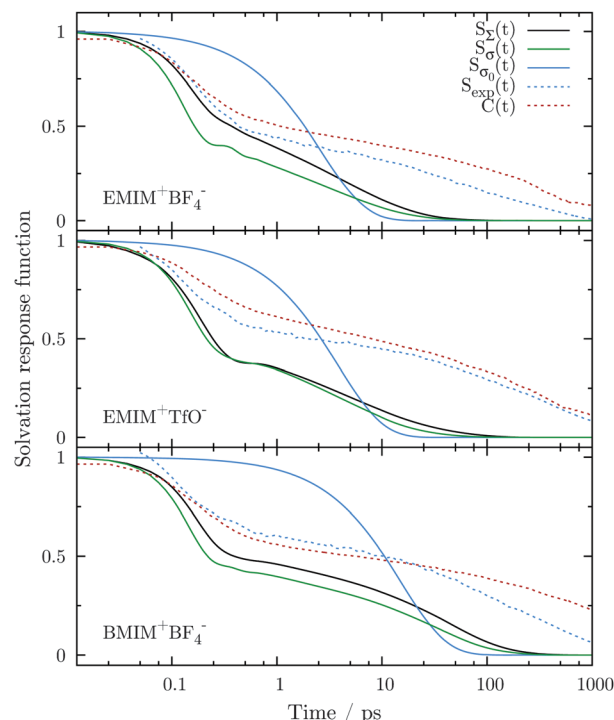


Fig. 2 Comparison of  $S_{\Sigma}(t)$  (black, cf. eqn (18)),  $S_{\sigma}(t)$  (green, cf. eqn (46)),  $S_{\sigma_0}(t)$  (blue, cf. eqn (44)),  $C(t)$  (dotted red, cf. eqn (57)) and experimental data<sup>7</sup> (dotted light blue). While  $S_{\sigma_0}(t)$  is a simple mono-exponential curve,  $S_{\sigma}(t)$  shows the typical differentiation into two distinct time domains. The addition of rotational motion in  $S_{\Sigma}(t)$ , i.e. taking whole  $\Sigma(\omega)$ , changes the curve only slightly. Comparison to  $S_{\text{exp}}(t)$  (cf. ref. 7) and  $C(t)$  shows that the solvation response function predicted by the RFCM decays too fast.

(cf. eqn (50)) only to a minor degree, except for the change in  $\beta$  in the case of  $\text{EMIM}^+\text{TfO}^-$ . This shows in a compact way the importance of  $\varepsilon(\omega)$  for  $\text{EMIM}^+\text{TfO}^-$ , which is evident from its spectrum in Fig. 1.

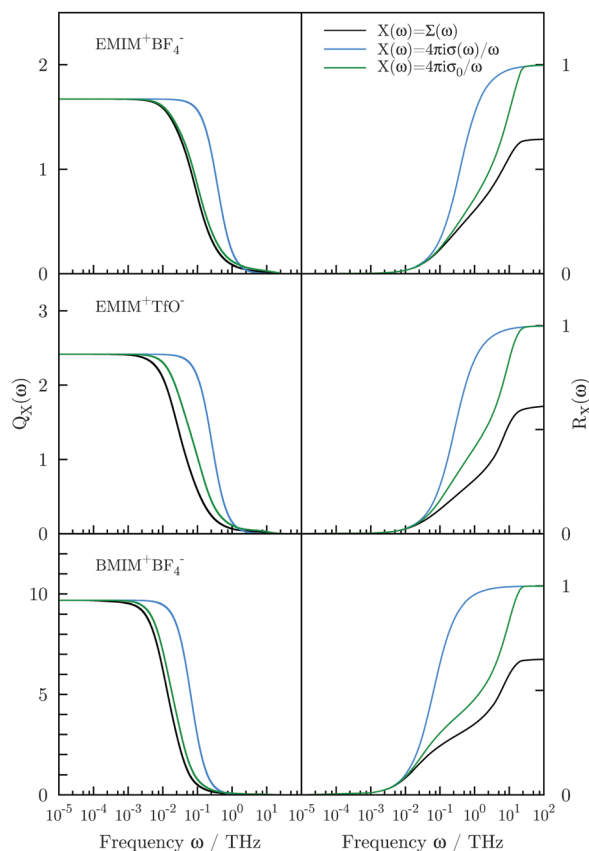
**2. The mean relaxation time.** The qualitative description of the time dependence of  $S(t)$  given above is now accompanied by a quantification in terms of the mean relaxation time  $\tau$  (cf. eqn (21), (22) and (34)). Thus, for the calculation of  $\tau$  one needs the time integral of  $\Delta U(t)$ , which corresponds to the zero-frequency limit in eqn (23), as well as the amplitude  $\Delta U(0)$ , given by the integral in the frequency domain (see eqn (34)). The respective integrand

$$Q_X(\omega) = \frac{1}{\omega} \frac{X(\omega)}{X(\omega) + 1 + \frac{\varepsilon_c}{2}} \quad (53)$$

and its running integral

$$R_X(\omega) = \int_0^{\omega} Q_X(\omega') d\omega' \quad (54)$$

are shown in Fig. 3 for the three cases  $X(\omega) = \{\Sigma(\omega), 4\pi i\sigma(\omega)/\omega, 4\pi i\sigma_0/\omega\}$ . The integrands in the left column of Fig. 3 are different, but their zero-frequency limit, i.e. the time integral  $T$ , is the same. This confirms numerically the analytical results found in Sections IIB and IIC. The running integrals  $R_X(\omega)$  are shown on the right-hand side of Fig. 3. Their asymptotic limits



**Fig. 3** The left column shows the integrands  $Q_X(\omega)$  with  $X(\omega) = \{\Sigma(\omega), 4\pi\sigma(\omega)/\omega, 4\pi\sigma_0/\omega\}$  (cf. eqn (53)). The zero-frequency limit corresponds to the time integral  $T$  (see eqn (22)). The right column shows the running integral  $R_X(\omega)$  of the corresponding curves in the left column (see eqn (54)). The last values of these integrals correspond to  $\Delta U_X(0)$  and are the amplitudes in eqn (21).

give the amplitudes  $\Delta U_X(0)$ . In accordance with Section IIC,  $\Delta U_{\sigma_0}(0)$  and  $\Delta U_{\sigma}(0)$  both are unity and  $\Delta U_{\Sigma}(0)$  can be calculated from eqn (37), which can be rewritten as

$$\frac{1}{\Delta U_{\Sigma}(0)} = \frac{\epsilon_c + 2\epsilon_{\infty}}{\epsilon_c + 2} \quad (55)$$

$$= 1 + \frac{2(\epsilon_{\infty} - 1)}{\epsilon_c + 2}. \quad (56)$$

In a system consisting of non-polarizable molecules, *i.e.*  $\epsilon_{\infty} = 1$ , the amplitude also becomes  $1/\Delta U_{\Sigma}(0) = 1$ . Consequently, at all three levels of complexity the mean relaxation time becomes the same. In the present case, though, the simulations were performed using a polarizable force field characterized by the following optical dielectric constants  $\epsilon_{\infty}$ : 1.749 (EMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup>), 1.906 (EMIM<sup>+</sup>TfO<sup>−</sup>) and 1.742 (BMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup>). This leads to amplitudes lower than 1 (see Fig. 3) and thus enhances the mean relaxation times by about 40–50%. Inspecting eqn (56) shows that only the asymptotic value of  $\epsilon(\omega)$  enters the amplitude. Thus, the complete spectrum  $\epsilon(\omega)$  is diminished by the dielectric conductivity  $4\pi i\sigma(\omega)/\omega$ , when considering the mean relaxation time.

The mean relaxation times of  $S_{\sigma_0}(t)$  and  $S_{\sigma}(t)$  are identical, as both the time integral  $T$  as well as the amplitudes are equal (see Fig. 3). In other words, the static conductivity describes  $S_{\sigma}(t)$  exactly on the average, but not in detail.

**3. Comparison to simulated and experimental solvation response functions.** So far, our considerations of the solvation response function were limited to the framework of the reaction field continuum theory. Now, we contrast these results with experiment<sup>7</sup> and simulation. In the latter case, we do not refer to the non-equilibrium simulation, but we have calculated<sup>10</sup> the solvation response function from equilibrium molecular dynamics (MD) simulation data as the time correlation function

$$C(t) = \frac{\langle \delta\Delta U(0)\delta\Delta U(t) \rangle}{\langle \delta\Delta U(0)^2 \rangle}, \quad (57)$$

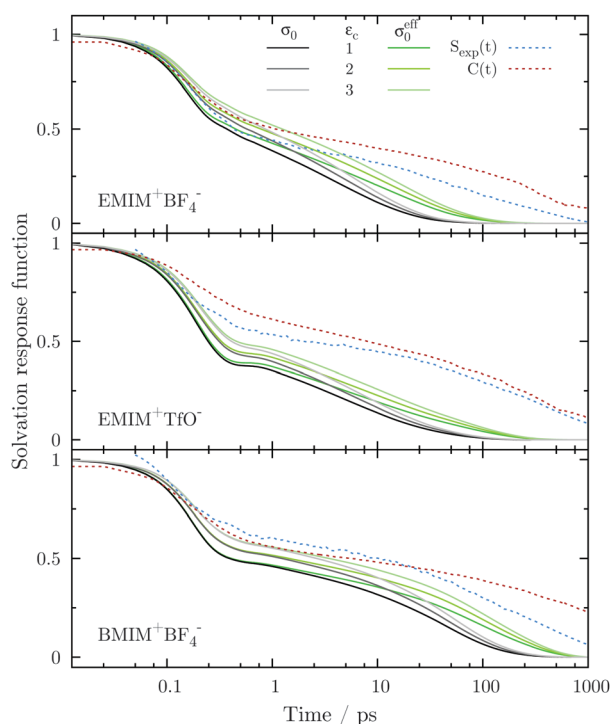
where  $\delta\Delta U(t)$  describes the fluctuations of the solvation energy difference between the two electronic states of the solute. The results are shown in Fig. 2 in comparison to the triple of continuum-based functions and experimental data.<sup>7</sup> The pair of the directly calculated functions  $C(t)$  (see eqn (57)) and those computed indirectly *via* inserting simulated dielectric spectra into the reaction field continuum model behave much like their experimental analogues (*cf.* Fig. 9 of ref. 7): the simple continuum model gives a solvation response function with the characteristic separation into two time regimes. The fast-decaying sub-picosecond regime of the solvation response is modeled rather well for EMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup> and BMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup>, but not for EMIM<sup>+</sup>TfO<sup>−</sup>, while the long-time regime is decaying much too fast in all three liquids. The striking similarity of curves derived from either the experimental or computational spectra demonstrates that deviations are almost independent of the source of the dielectric spectrum, but rather show up the limitations of the reaction field continuum model. Table 1 lists the fit parameters used to describe the various solvation response functions calculated from the continuum model in comparison to the linear response time correlation function used in ref. 10 and experimental data.<sup>7</sup>

**4. Retarding relaxation within the framework of RFCM.** Both in simulation and experiment,<sup>7,32</sup> RFCM correctly models the dualistic shape of the solvation response function in a qualitative way. However, at the quantitative level clear deficiencies of the model theory are visible. In particular, in the long-time regime the solvation response function decays too fast. Eqn (33) and (45) offer a possibility for retardation. The time integral  $T_X$  represents the area under the curve  $\Delta U_X(t)$  and is thus proportional to the mean relaxation time. For a monotonic time function, any enhancement of its integral automatically elevates the whole curve. Therefore, the parameters  $\epsilon_c$  and  $\sigma_0$  entering  $T_X$  are a direct route to manipulate  $S(t)$  both in its shape and its integral properties. At the experimental side an effective conductivity  $\sigma_0^{\text{eff}} = \frac{\sigma_0}{2.4}$  was determined for a series of ionic liquids.<sup>6,32</sup> In order to be consistent with these findings, we use the same scaling factor here. The results are shown in Fig. 4 (green curves). A further deficiency of the RFCM is the

fact that structural and electrostatic properties of the solute do not enter at all, if  $\epsilon_c = 1$ , meaning that the solute is not polarizable. An increase in  $\epsilon_c$  corresponds to enhancing the polarizability of the solute. Assembling the molecular polarizability of C153 from its atomic polarizabilities according to ref. 51 and converting it to  $\epsilon_c$  via the Clausius–Mosotti equation we get a tentative value of  $\epsilon_c = 3$ . Therefore, Fig. 4 shows curves for the triple  $\epsilon_c = 1, 2, 3$ . The value  $\epsilon_c = 2$  was included, because it was used in experimental studies.<sup>6–9,32</sup>

As can be seen in Fig. 4, both a higher  $\epsilon_c$  as well as using  $\sigma_0^{\text{eff}}$  instead of  $\sigma_0$  leads to an elevation of  $S(t)$ . However, the influence of  $\epsilon_c$  is focused on short and medium times, while  $\sigma_0^{\text{eff}}$  mainly affects the long-time domain. Thus, simultaneously increasing  $\epsilon_c$  and using  $\sigma_0^{\text{eff}}$  allows us to manipulate  $S(t)$  in the whole time scale. The best example is  $\text{BMIM}^+\text{BF}_4^-$ , where  $\sigma_0^{\text{eff}}$  combined with  $\epsilon_c = 3$  gives reasonable agreement with experimental curves. A similarly good agreement is found in the case of  $\text{EMIM}^+\text{BF}_4^-$ , while for  $\text{EMIM}^+\text{TfO}^-$  the improvement is largely confined to the initial region of  $S(t)$ .

Table 1 lists the fit parameters and mean relaxation times  $\tau_X$  (last column) for  $S_\Sigma(t)$  as a function of  $\epsilon_c$  and  $\sigma_0$ . A stringent feature across the three liquids studied here is that the variation in  $\epsilon_c$  and/or  $\sigma_0$  primarily affects  $\tau_2$ , while  $\beta$  and the amplitude  $a$  stay almost constant and  $\tau_1$  shows only modest change. Although numerically evaluated the mean relaxation times  $\tau_X$  exactly follow eqn (38). Approximately,  $\tau_2$  also follows



**Fig. 4** Variation of  $\epsilon_c$  from 1 to 3 in combination with  $\sigma_0$  (black curves) or  $\sigma_0^{\text{eff}} = \sigma_0/2.4$  (green curves; for the factor 2.4, cf. ref. 6, 9 and 32) in comparison to results from simulation<sup>10</sup> (red dotted line) and experiment<sup>7</sup> (blue dotted line). Increasing  $\epsilon_c$  lifts the curves mainly for short and medium times, while using  $\sigma_0^{\text{eff}}$  instead of  $\sigma_0$  slows down the decay in the long-time domain.

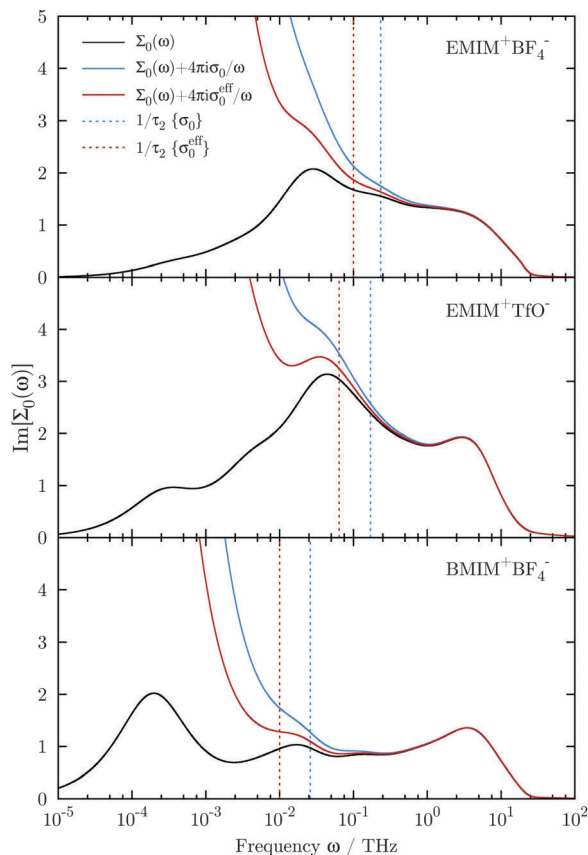
this relation. However, this comes from the special values of parameters  $\beta$  and  $a$ . For the KWW part of the fit function the contribution to the mean relaxation time is given by  $\langle\tau\rangle = ((1 - a)/\beta)\Gamma(1/\beta)\tau_2$ . If  $\beta$  and  $a$  are close to 0.5, as is the case of  $\text{EMIM}^+\text{BF}_4^-$  and  $\text{EMIM}^+\text{TfO}^-$ ,  $\tau_X \approx \tau_2$ .

**5. Linking the time behaviour of  $S(t)$  with the imaginary part of the dielectric spectrum.** Although usually subtracted, the conductivity hyperbola  $4\pi i\sigma_0/\omega$  is an essential feature of the imaginary part of the dielectric spectrum of conducting systems. Within the framework of RFCM, we have learned above in eqn (41) that the conductivity hyperbola has to be included to avoid divergence of the time integral. As can be seen in Fig. 5 this has dramatic consequences for  $\text{Im}[\Sigma(\omega)] = \Sigma''(\omega)$ : in the low-frequency region of the spectrum the intrinsic part  $\Sigma_0(\omega)$  is completely swamped by the hyperbola, as its values exceed those of  $\Sigma_0(\omega)$  by many orders of magnitude. The effect that the peaks at low frequencies do not significantly contribute to the RFCM can also be observed in Fig. 3, where the integrands in the left column begin to differ only beyond a certain frequency threshold and the zero-frequency limit is determined only by the static conductivity (cf. eqn (29)–(33) and (45)). In contrast, this is not the case in the high-frequency region of the spectrum, which is the same for  $\Sigma_0(\omega)$  and  $\Sigma(\omega)$ . Here, the characteristic feature of the spectra of all three systems is a peak at  $\approx 4$  THz. In the time domain this corresponds to a relaxation time of  $\approx 0.25$  ps. This value is close to the  $\tau_1$  values in Table 1, which show only modest variation across systems and model parameters.

As illustrated by Fig. 5 a threefold partitioning of the frequency range is possible:  $\Sigma(\omega) \gg \Sigma_0(\omega)$ ,  $\Sigma(\omega) \approx \Sigma_0(\omega)$  and  $\Sigma(\omega) = \Sigma_0(\omega)$ , classified as low, medium and high in the following. In this medium region, the fine structure of  $\Sigma_0(\omega)$  emerges to an extent depending on the value of the static conductivity. Using  $\sigma_0^{\text{eff}}$  instead of  $\sigma_0$  shifts the medium region towards lower frequencies. Consequently, characteristic features of  $\Sigma_0(\omega)$  become noticeable in  $\Sigma(\omega)$ . This goes along with the retardation of  $S(t)$  (cf. Fig. 4), which can be focused on  $\tau_2$ , as we have learned above (cf. Table 1). We emphasize that  $\tau_2$  and (the almost constant)  $\beta$  from the KWW part of the fit function describe a stretched exponential representing the superposition of many exponentials. The corresponding frequency  $\omega_2 = 1/\tau_2$  is given as a vertical dotted bar in Fig. 5 for  $\sigma_0$  and  $\sigma_0^{\text{eff}}$  with  $\epsilon_c = 1$ . In fact,  $\omega_2$  marks the beginning of the high-frequency region, where the differences between  $\Sigma_0(\omega)$  and  $\Sigma(\omega)$  have disappeared. When using  $\sigma_0^{\text{eff}}$  instead of  $\sigma_0$ ,  $\omega_2$  shifts downwards synchronously with the conductivity hyperbola.

Taking the arguments above together, one understands why the RFCM produces reasonably good agreement in the short-time regime, while decaying too fast for longer times. In particular, in the case of  $\text{EMIM}^+\text{TfO}^-$ ,  $\Sigma(\omega)$  lacks spectral information of  $\Sigma_0(\omega)$  across a wide frequency range, which cannot be repaired sufficiently by rescaling  $\sigma_0$ . As the latter is considerably lower for  $\text{BMIM}^+\text{BF}_4^-$  when compared to the other two systems, a wider range of the spectrum is covered by  $\Sigma(\omega)$ . Therefore, in this case RFCM agrees much better with simulation and experiment.

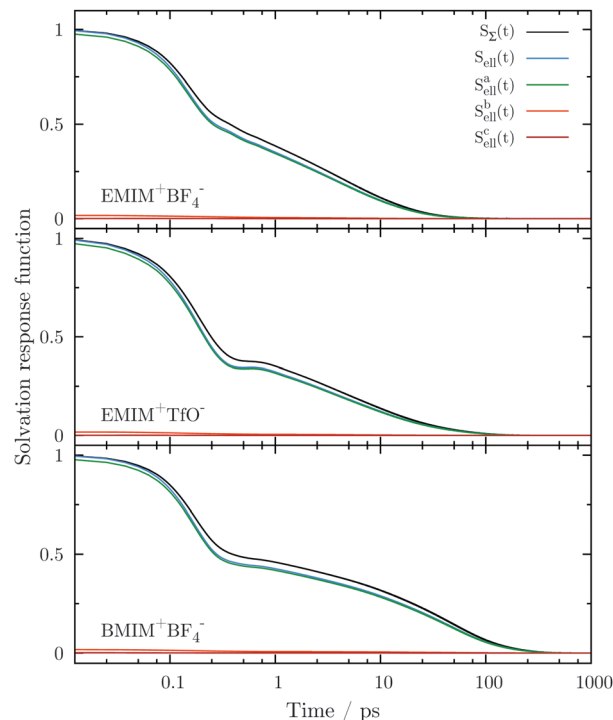




**Fig. 5** The imaginary part of  $\Sigma_0(\omega)$  by itself (black curve) and after addition of the conductivity hyperbola using either the unscaled  $\sigma_0$  (blue curve) or the scaled  $\sigma_0^{\text{eff}} = \sigma_0/2.4$  (red curve). The two curves including the static conductivity diverge quickly as  $\omega$  becomes smaller. The fine structure of the peaks at low frequencies ( $\omega < 10^{-2}$  THz) is quickly diminished by the hyperbola, especially as this graph is plotted on a semilog scale. The vertical dotted lines mark  $\omega_2 = 1/\tau_2$ , when either using the unscaled conductivity  $\sigma_0$  (dashed blue line) or the scaled  $\sigma_0^{\text{eff}}$  (dashed red line).

### C. Anisotropy in charge distribution and shape

All above considerations refer to dipolar solute enclosed in a spherical cavity. Within the RFCM the dipole moment and the radius of the sphere are, except for  $\epsilon_c$ , the only parameters describing the solute. As they both enter as prefactors, they cancel out upon normalization. In order to include more detailed features of the solute, we modified RFCM in two ways. First, the steric anisotropy of the solute was modeled by replacing the spherical cavity with an ellipsoid,<sup>39,43</sup> resulting in eqn (49). The principal axes of the solute were aligned with the coordinate system and a bounding box parallel to these axes was erected. This gave the relative lengths of the axes  $a$ ,  $b$  and  $c$  of the ellipsoid. Subsequently,  $a$ ,  $b$  and  $c$  were rescaled so that the volume of the ellipsoid equaled the Voronoi volume of C153, yielding  $a = 7.00$  Å,  $b = 4.66$  Å and  $c = 2.85$  Å. The corresponding ellipsoidal shape factor integrals<sup>41</sup> are  $A_a = 0.18$ ,  $A_b = 0.30$ ,  $A_c = 0.52$ . The change in dipole moment upon excitation  $\Delta\vec{\mu}$  of the solute was projected onto the principal axes, giving the components  $\Delta\mu_a = -1.24$  eÅ,  $\Delta\mu_b = 0.12$  eÅ,  $\Delta\mu_c = -0.02$  eÅ. Since  $\Delta\mu_a$  exceeds  $\Delta\mu_b$  by an order of magnitude



**Fig. 6** Solvation response function using the model with an ellipsoidal cavity. The black curve shows the response using a spherical cavity. The total response with an ellipsoidal cavity in blue, the contribution of the principal component a in green, the contribution of the principal component b in orange and the contribution of the principal component c in red.

and  $\Delta\mu_c$  by another one, the dipolar energy is essentially given

by the prefactor  $\frac{\Delta\mu_a^2}{abc}$ . The only difference to the spherical cavity comes from  $A_a \neq \frac{1}{3}$ . As can be seen in Fig. 6 and Table 1, the deviations from the spherical model are marginal. Table 1 rationalizes that the  $a$ -axis of the ellipsoid essentially determines the time dependence as a whole. This comes from the fact that the  $a$ -axis and  $\Delta\vec{\mu}$  are almost collinear. Thus, the solute behaves as if it were spherical.

A second possibility of including anisotropic features of C153 is the inclusion of higher multipole moments of the solute in the RFCM, see eqn (3). We have included the quadrupole moment, although changes were marginal as well (data not shown).

## V. Conclusion

The bases of our investigations are the simulated spectra of three selected ionic liquids, EMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup>, EMIM<sup>+</sup>TfO<sup>−</sup> and BMIM<sup>+</sup>BF<sub>4</sub><sup>−</sup>, differing in the relative weighting of translation (dielectric conductivity) and rotation (dielectric permittivity). As we used a polarizable force field, the behaviour at optical frequencies could be extrapolated. The simulated spectra were converted to the solvation response function  $S(t)$  within the framework of the reaction field continuum model. While experiments cannot separate the contributions from translation and rotation, simulated spectra allow for a detailed analysis in this regard.

Our findings can be summarized as follows. If one would use the dielectric spectra in the usual way, *i.e.* without the conductivity hyperbola, the formalism of the RFCM diverges, which was shown in particular for the mean relaxation time. Therefore, inclusion of the static conductivity is essential. Taken alone, it would give a mono-exponential solvation response function. Proceeding from the static to the frequency-dependent conductivity gives a qualitatively correct shape of  $S(t)$ . Taking the whole  $\Sigma(\omega)$ , which also includes rotation, only marginally changes the shape of the function. This shows very clearly the dominant role of conductivity, *i.e.* of translational motion, a feature already encountered in previous studies.<sup>6,7,10,32,34</sup>

In accordance with experimental studies,<sup>6–9,32</sup> our simulations confirm that the RFCM predicts a too fast decay of  $S(t)$  at longer times. We found that this can be traced back to a fundamental property of the dielectric behaviour of conducting systems. In the low-frequency region of the imaginary part of  $\Sigma(\omega)$  the conductivity hyperbola  $4\pi i\sigma_0/\omega$  suppresses the fine structure of all other contributions represented by  $\Sigma_0(\omega)$ . Generally, we used a fit function comprised of a mono-exponential describing the short-time regime and a KWW function representing the long-time behaviour. The inverse  $1/\tau_2$  of the KWW relaxation time marks the onset of the region of divergence between  $\Sigma(\omega)$  and  $\Sigma_0(\omega)$ .

For non-polarizable systems, where  $\epsilon_\infty = 1$ , the mean relaxation time of  $S(t)$  is exactly the same, irrespective of the level of complexity,  $4\pi i\sigma_0/\omega$ ,  $4\pi i\sigma(\omega)/\omega$  or  $\Sigma(\omega)$ . It is exclusively determined by the inverse of  $\sigma_0$  as well as by the value of the cavity dielectric constant  $\epsilon_c$ . Adapting these parameters, the resulting  $S(t)$  can be improved not only in its integral properties, but also in its functional shape. However, this remedy is only partially successful and depends on the system under consideration. We suggest that the extent of improvement depends on the size of that portion of the imaginary part of  $\Sigma_0(\omega)$  that is suppressed by the conductivity hyperbola. In fact, for EMIM<sup>+</sup>TfO<sup>−</sup> the deviations are the largest.

In the RFCM all parameters except for  $\epsilon_c$  characterizing the solute cancel out upon normalization. We have tried to introduce more solute-specific features by considering the anisotropy of the solute in the shape and charge distribution. The spherical cavity was replaced by an ellipsoid and the dipole moment was augmented by the quadrupole moment. However, within the RFCM anisotropic features of the solute do not create substantial changes in  $S(t)$ .

## Acknowledgements

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