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Responses to referee reports for
"Multiscale response of ionic systems
to a spatially varying electric field".

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First, I sincerely thank the referee for her/his fruitful comments. I have addressed all points made below.

1. The referee raises a very good question. It is a fundamental interesting point to discuss when separation of variables is valid. However, to keep the focus of the paper this is sentence is removed as it is not important for the treatment. What is important is that the temporal part is a delta function which is true when the system is in a steady state. The text has been changed to highlight this, page 4.

2. The sentence is removed.

3. I see the point and I agree with the referee that a comment about the dielectric constant (or relative permittivity) is helpful. The Debye-Hückel regime defined by the T_∞-system is a special case: The ions have no electrostatic interactions, thus placing two interacting test charges corresponds to them being placed in vacuum (or no-screening medium) thus $\epsilon = 1$ and is wavevector independent.

   This cannot be inferred from the equation given in the response. In my understanding the argument is the other way around for the screening regime: From Hansen and McDonald (3rd edition) Eqs. (10.2.8) and (10.2.11) we have

   $$\frac{1}{\epsilon(k)} = 1 - \frac{4\pi n e^2}{k_B T k^2} S_{zz}(k)$$

   In the perfect screening regime it is known that $\epsilon(k) \to \infty$. This is an experimental fact (Hansen and McDonald, p. 297), albeit the Stillinger-Lovett sum rules can be used in the case of perfect screening, but not in general. This means $4\pi n e^2 S_{zz}(k)/(k_B T k^2) \to 1$ which in turn implies $S_{zz}(k) \propto k^2$ in the $k \to 0$ limit.

   In the revised manuscript it is now stated that the relative permittivity is unity for the T_∞-system, page 6.

4. I am not sure I understand this point. Substituting Eq. (18) from the manuscript into the equation above

   $$\frac{1}{\epsilon(k)} = 1 - \frac{8\pi e^2}{D_0 k^2} \widetilde{\chi}(k)$$

   Notice the negative sign on the second term. $D_0 > 0$ and $\widetilde{\chi}(k) > 0$ thus $\epsilon(k) > 1$ as expected. Is the confusion rooted in the response function $\chi_{ZZ}(k) = -n S_{zz}(k)/(k_B T)$ introduced by Hansen and McDonald and the (different) response function χ introduced in this work?

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5. First, the constitutive relation comes from Eq. (7). Consider are system where the potential gradient is negative at some point z_0. Here the cations will flow (i.e., there will be a mass flux) in the positive z-direction as given by second term in Eq. (7). If the ion is an anion it will migrate in the opposite direction.

   In Eq. (10) the ion charge q is negative for anions and positive for cations and $\tilde{n}_i(k) \propto -\widetilde{\chi}_i(k)/q$. In the monovalent case we then see from Eqs. (11) and (13) that the density profiles for the two ions oscillate around the horizontal line n_0. One profile is a mirror image of the other around that line. This is now highlighted in the revised manuscript, page 5. Also, additional comments on the differences between χ and S_{zz} is given in the conclusion section.

6. The referee is absolutely right - this has been corrected.

7. Very important point raised by the referee. The reason is a matter of computational speed; the shifted force method is much faster than any of the techniques based on the Ewald summation method.

   First, the maximum screening length is for the T_∞-system where in reduced units $\lambda_D = \sqrt{\epsilon T} \approx 1.6$, hence, $\lambda_D < 1.6$ for all systems. The cut-off is therefore around twice the screening length. The cut-off for the van der Waals interactions is quite large (the force is in the order of 10^{-6} at the cut-off distance), but is simply used here to reduce the number of simulation parameters.

   Indeed the shifted-force (SF) method may be questionable for non-inform systems. Especially, it will fail for confined systems - and so will the standard Ewald methods. There are, however, strong indications that the SF method applies here: (i) the same results were found by letting $r_c = 6$ for selected situations, i.e., twice the cut-off distance. This simple check is always carried out. (ii) Comparing the non-equilibrium (i.e non-uniform) data with the predictions from the (uniform) linear response theory gives good agreement, Fig 4 b, also indicating that the SF method is applicable.

   This concern is raised by both referee. To ensure that the SF method applies new simulations are carried out carefully comparing data using this method with data using the direct Ewald summation method. In the Ewald summation method the interaction energy is

   $$V = \frac{1}{2} \sum_{\mathbf{n}} \sum_{ij} \frac{q_i q_j}{|\mathbf{r}_{ij} + L\mathbf{n}|}$$

   $\mathbf{n}$ is an integer vector accounting for the replica systems. This direct method is not usually applied as the convergence is slow, however, for this particular simple and small system convergence is achieved quite quickly as seen in figure 4; using 124 replica systems suffices. This result is not surprising and is discussed in Refs. 16 and 17 in the manuscript; in Ref. 17 other properties are also compared.
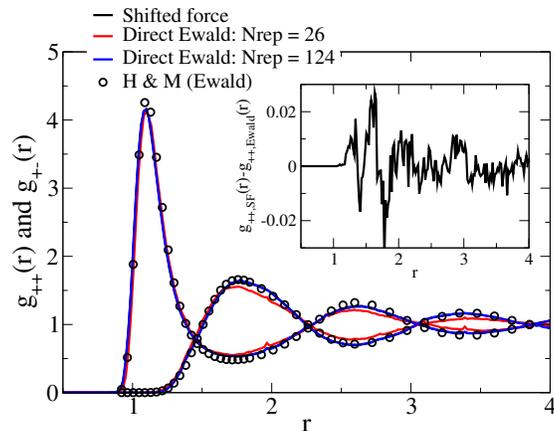
Figure 1: Radial distribution function for the molten salt system for the SF method and Ewald method using a different number of replica systems, N_{rep}. Also shown are the data points from Hansen and McDonald, Ref. 1 in the manuscript. The inset shows the difference between the SF and the Ewald method for N_{rep}=124 as this is not clear from the main figure.

Figure 5 shows an example for the charge density profile using the SF and Ewald methods in the non-equilibrium situation. Also, the corresponding spectra are shown. Clearly, the agreement is satisfactory.

A paragraph justifying the application of the SF method is now included in the simulation details section.

This reply is copied in my response to the other referee.

8. Again a very good point! The choice to remove the Coulomb interactions rather than simply increase the temperature is a matter of numerical stability. By removing the Coulomb interactions one can be sure to have $k_B T \gg q\phi$ fulfilled, corresponding to a relative permittivity of unity. This is, in principle, only achieved by letting the temperature be infinite if the Coulomb interactions are included.

The referee is correct: It is a van der Waals fluidic system, but it responses to an external electric field which is what the work investigates. The justification for including this is to compare the single particle diffusion to the electric field response.

A sentence highlighting this point is included in the manuscript, page 7.

9. Indeed! Yurukawa is changed to Yukawa throughout the manuscript.

10. I thank the referee for noticing this point. Somehow the word 'modified' disappeared in the manuscript editing. This is now highlighted. Also, the additional details for the model is presented as they should be.
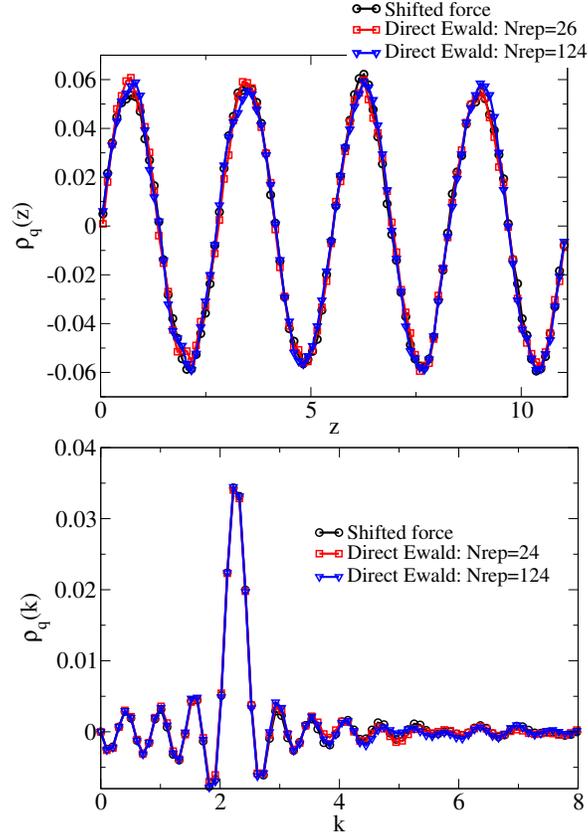
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Figure 2: Upper figure: Charge profile results for the shifted force and Ewald methods. Lower figure: Corresponding spectra.

11. The fitting parameter values are now included in the figure caption of Fig 1.

12. First let me stress that $\widetilde{\chi}(k) \propto S_{zz}(k)$ only in the screening regime. In the Debye-Hückel regime $\widetilde{\chi} \propto \widetilde{D}(k)$.

The fundamental difference is that the χ-response function relates the *mass* flux to the external electric field *excluding* the contribution from the concentration gradient (here modelled through the self-diffusion). The charge-charge response function relates the *charge* density to the electric field; this *includes* effects due to concentration gradients.

It is of course very important that this is clear in the text, and I have rewritten the first paragraph in the conclusion and emphasized the difference on page 4 and in the conclusion.

13. The referee raises a very interesting point! First, from my understanding it requires extremely accurate simulation data to show that the sum rules are fulfilled; for example, Hansen and McDonald do not show this. To my knowledge only Ballenegger and Hansen [Mol. Phys., 102: 599 (2014)] show the first sum rule from simulation data.

    New simulations of the molten salt system are carried out using a bigger system size, $L = 20.1$, such that the radial distribution function is unity for large radii. Eq. (25) from the paper is then used to calculate the charge-charge structure, S_{zz}. This is plotted in Fig. 3 as a function of k^2 in the limit of small k. It is seen that the expansion of S_{zz} with respect
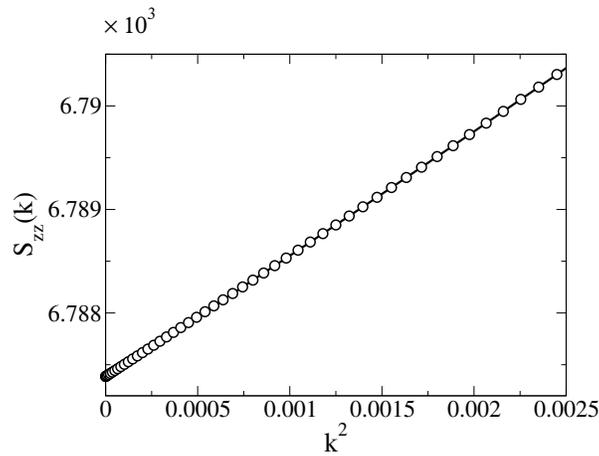

Figure 3: Charge-charge structure as a function of k^2.

    to k follows the expected k-dependence.

    Now, the first Stillinger-Lovett sum rule simply expresses charge neutrality; this is trivially fulfilled in the systems studied in this work. However, it can not be inferred from the sum rule that are based on the radial distribution functions. Ballenegger and Hansen write the charge neutrality condition as

$$n \int_0^\infty \delta g(r) r^2 dr = 0 \,.$$

    For the molten salt this integral yields approx 0.15. This is also tested using the data presented in Hansen and McDonald, Ref. 1, giving the same result.

    It would be very interesting to investigate this problem in great detail in future work.

14. The characteristic wavelength is given by $l = 2\pi/k_{max}$, where k_{max} is the wavevector where $\tilde{\chi}$ has its maximum (or peak). This is now written in the manuscript page 9-10.

15. I definitely agree with the referee that this is not surprising, yet it does stress the point that in the Debye-Hückel regime the underlying processes governing the self-diffusion (single particle property) are the same as the processes responsible for response when applying an external field. This also supports the discussion of Fig. 5.

    Simply from the form of $\tilde{\chi}$ for $T = 1.0177$ and $T = 0.0177$ one can immediately see that such collapse is not found here, hence, different processes govern the response. This is now stressed in the manuscript.

16. This has been corrected.

17. In this work only studies the case where the fundamental mode is excited. For T=0.0177 only $k < 12\pi/L$ is shown, for higher wavevectors higher order modes become excited (as stated on page 10) and Eq. (14) is not valid. This is now stressed further on pages 5 and 10.

18. Regarding Fig. 4 (b): The lines are predictions from the theory; reference to the equation is now provided.

    As it is stated in the text, Eqs. (13)-(18) do not apply, hence, for the ionic liquid system the response function is calculated from the Fourier coefficients for the densities and the zero wavevector diffusivity.