Response to Comments on “Molecular Dynamics Simulation of the Surface Tension of Aqueous Sodium Chloride: from Dilute to Highly Supersaturated Solutions and Molten Salt” by Wang et al.

Dear Editor,

Many thanks for the kind effort guiding our manuscript through the peer review process. We would also like to thank the reviewers and Dr. W. R. Smith for the valuable and constructive comments, which help us improving the manuscript. Listed below are our point-by-point responses to the comments, including the corresponding changes made to the revised manuscript. The reviewer’s comments are marked in blue and our answers are marked in black, and the revision in the manuscript in further formatted as ‘*Italics*’.

During the manuscript revision, we discovered an error in the submitted manuscript when using the pressure tensor method to calculate surface tension (please find more details below). We sincerely apologize for it. The results have been corrected in the revised manuscript and our major finding and conclusions remain unaffected. Besides, we updated the method to determine the excess surface entropy and enthalpy of molten NaCl at 298.15 K according to the recent literature findings (Sega et al. 2018).

Thank you and best regards,
Xiaoxiang Wang
On behalf of all co-authors

Technical correction

We discovered an error in the submitted manuscript when using the pressure tensor method to calculate surface tension. Based on the diagonal component of the pressor tensors (P_{xx}, P_{yy}, P_{zz}) from Molecular Dynamics (MD) simulations, the correct equation to calculate the surface tension should be Eq. R1 (Eq. 1 in the submitted and revised manuscript). However, we mistakenly applied a negative $<P_{zz}>$ instead of a positive one (marked in red in Eq. R2) when processing the pressor tensors data. Here <…> refers to the time average. For double check, all cases have been re-simulated and the results have been corrected in the revised manuscript. Since the absolute value of $<P_{zz}>$ is much smaller than $<P_{xx}>$ and $<P_{yy}>$ in general, the corrections to the surface tension values are relatively small (Table R1 and Figure R1) and our major finding and conclusions remain unaffected.

$$\sigma_{MD} = 0.5L_z[\langle P_{zz}\rangle - 0.5(\langle P_{xx}\rangle + \langle P_{yy}\rangle)] \qquad \text{(Eq. R1)}$$

$$\sigma_{MD} = 0.5L_z[-\langle P_{zz}\rangle - 0.5(\langle P_{xx}\rangle + \langle P_{yy}\rangle)] \qquad \text{(Eq. R2)}$$

Table R1. Comparison of the corrected values of surface tension (with Eq. R1) in the revised manuscript and the ones (with Eq. R2) in the submitted manuscript.

NO.	x_{NaCl} in bulk region	Corrected surface tension (mN m^{-1})	Surface tension in the submitted manuscript (mN m^{-1})	NO.	x_{NaCl} in bulk region	Corrected surface tension (mN m^{-1})	Surface tension in the submitted manuscript (mN m^{-1})
1	0	62.24±0.044	61.9±0.02	12	0.36	84.35±0.143	79.58±0.38
2	0.037	63.48±0.03	63±0.24	13	0.384	85.67±0.183	79.31±0.32
3	0.067	64.8±0.014	63.9±0.14	14	0.409	86.9±0.04	80.22±1
4	0.123	67.41±0.089	66.23±0.1	15	0.44	87.83±0.25	80.39±1.01
5	0.156	69.49±0.006	67.56±0.17	16	0.47	88.03±0.88	79.9±0.78
6	0.184	70.76±0.1	68.93±0.06	17	0.504	88.77±0.42	80.73±1.5
7	0.219	73.61±0.055	70.67±0.1	18	0.54	90.35±0.6	81.93±2.12
8	0.261	76.06±0.14	73±0.087	19	0.59	93.4±2.157	83.42±1.17
9	0.283	77.5±0.11	73.93±0.37	20	0.61	97.6±1.46	84.23±1.18
10	0.304	79.7±0.19	75.8±0.25	21	0.64	102.53±0.46	87.1±1.73
11	0.334	82.06±0.25	78.13±0.73	22[a]	0.4018	86.9±0.59	79.1±0.51

a. The solution slab in this system is 3 nm × 3nm × 10 nm and the simulation box is 3 nm × 3nm × 30 nm.

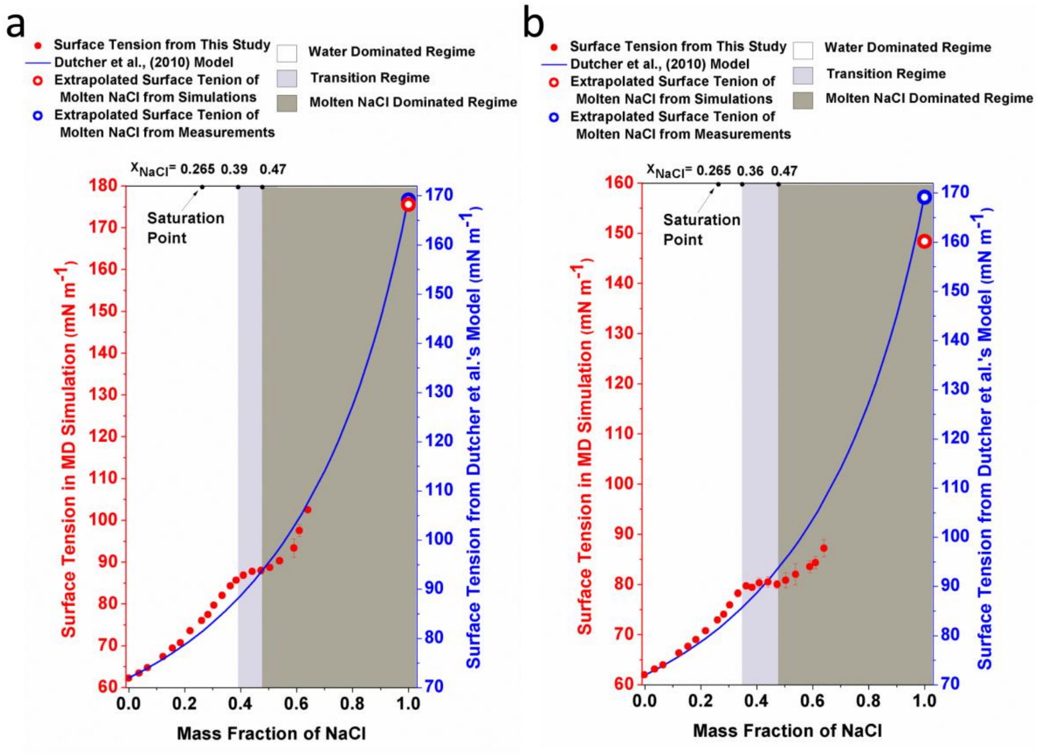

Figure R1. Surface tension of aqueous NaCl solution at different concentrations. (a) the corrected Figure 4a with Eq. R1 and (b) the original version with Eq. R2 in the submitted manuscript.

Updated method to determine entropy and enthalpy of the molten NaCl at 298.15 K

There are three ways to calculate the excess surface entropy, i.e. the direct method, the numerical derivative and the derivative of temperature-surface tension ($\mathrm{T}-\sigma$) relation. Descriptions about these three methods are summarized in the Table R2. In our paper, we calculated the excess surface entropy by the direct method (1) at 298.15 K for NaCl solution up to mass fraction (x_{NaCl}) of ~ 0.64 (Fig. 6) and (2) at high temperature of 1000 to 1700 K for molten NaCl, from which the excess surface entropy of molten NaCl at 298.15 K was extrapolated (original Fig. 5b). However, a very recent paper (Sega et al., 2018) compared these three methods in determining the excess surface entropy of liquids and found that the direct method might not be applicable at high temperature because of its significant deviations to the excess surface entropy derived with the derivative of $\mathrm{T}-\sigma$ relation when the temperature is high. We thus carefully checked the excess surface entropy of molten NaCl at 1000-1700 K determined from the direct method in our study. Fig. 5a shows an almost perfect linear relationship between the MD simulated surface tension of molten NaCl and temperature between 1000-1700 K ($\sigma_{\mathrm{molten\ NaCl}}(\mathrm{T}) = -0.0755 \times \mathrm{T} + 198.09$). Following Dutcher et al. (2010), we thus performed a linearly extrapolation to these data to obtain the surface tension of molten NaCl at the room temperature (298.15 K). Since $\sigma_{\mathrm{molten\ NaCl}}(\mathrm{T}) = -0.0755 \times \mathrm{T} + 198.09$, by performing the derivative of $\mathrm{T}-\sigma$ relation ($\frac{\Delta \mathrm{S(T)}}{\mathrm{A}} = \frac{-d\sigma(\mathrm{T})}{d\mathrm{T}}$, Table R2), we can obtain an excess surface entropy ($\frac{\Delta \mathrm{S}_{\mathrm{molten\ NaCl}}}{A}$) equals to 0.0755 mN m^{-1} K^{-1}. This value is quite different from the slope of the data in Fig. 5b, which indicates that Sega et al. (2018)'s conclusions are also applied to our case. Therefore, we abandoned Fig. 5b in the revised manuscript. The excess entropy term ($T \cdot \frac{\Delta \mathrm{S}_{\mathrm{molten\ NaCl}}}{A}$) of the molten NaCl at 298.15 K is directly calculated by multiplying the $\frac{\Delta \mathrm{S}_{\mathrm{molten\ NaCl}}}{A}$ ($= 0.0755$ mN m^{-1} K^{-1}) by the temperature of 298.15 K. The entropy and enthalpy terms at NaCl mass fraction of 1.0 in Fig. 6 have thus been updated.

Note again that the majority of data in Fig. 6 (except the points for x_{NaCl} of 1.0) are obtained by the direct method at 298.15 K. We also performed independent calculation of the excess surface entropy and enthalpy of pure water at temperatures from 278.15 K to 348.15 K based on the aforementioned three methods (in Table R2). As shown in Figure R2 (Fig. S1 in the supplement of the revised manuscript), results from these three methods well agree with each other, which means that results based on the direct method at room temperature can be trusted.

Corresponding to the changes in Fig. 5 and Fig. 6, the following text was added into Page 8 Line 9-14 to introduce these calculations. *"According to Fig. 5, we have* $\sigma_{NaCl} = -0.0755 \cdot T + 198.09$*, then we can get* $\frac{\Delta S_{NaCl}}{A}$ *= 0.0755 mN* m^{-1} K^{-1} *because of* $\frac{\Delta S(T)}{A} = \frac{-d\sigma(T)}{dT}$ *(Landau and Lifshitz, 1969). Therefore, for molten NaCl (*x_{NaCl} *= 1.0),* $\frac{T \cdot \Delta S_{NaCl}}{A}$ *at 298.16 K is 22.15 mN* m^{-1}*, and* $\frac{\Delta H_{NaCl}}{A}$ *at 298.15 K is 198.09 mN* m^{-1} *(Fig. 6). Here, we used the derivative of temperature-surface tension relation to calculate the excess surface entropy, and more discussions about the comparison of these methods can be found in the supplement (Fig. S1)".*

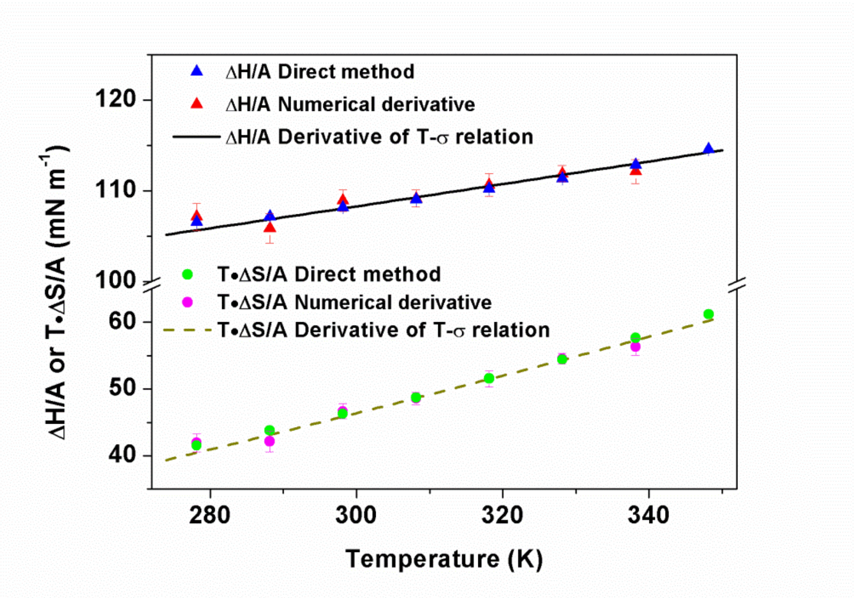

Figure R2. $\frac{\Delta H}{A}$ and $\frac{T \cdot \Delta S}{A}$ of pure water at temperatures from 278.15 K to 348.15 K obtained from different methods.

Table R2. Descriptions of different methods to calculate $\frac{\Delta H}{A}$ and $\frac{T \cdot \Delta S}{A}$.

1. The Direct Method

We simulated liquid layers with and without surfaces. The difference of enthalpy per area of liquid with surfaces and the one of liquid without surfaces is the excess surface enthalpy ($\frac{\Delta H}{A}$). And $\frac{T \cdot \Delta S}{A}$ can be then calculated as $\frac{T \cdot \Delta S}{A} = \frac{\Delta H}{A} - \sigma$.

2. The numerical derivative

We first calculated σ of the studied liquid at different temperatures, then we used the equation $\sigma(T) = \sigma(T_0) + a \times (T - T_0) + b \times (T - T_0)^2$ to fit the data of $\sigma(T_0)$, $\sigma(T_0 - 10\ K)$ and $\sigma(T_0 + 10\ K)$ to get the fitting parameters a and b for a given T_0, i.e., $a(T_0)$ and $b(T_0)$, respectively. As $\frac{\Delta S(T)}{A} = \frac{-d\sigma(T)}{dT}$, we have $\frac{\Delta S}{A}(T_0) = -a(T_0)$. And we can get $\frac{\Delta S}{A}$ at different temperature one by one. For $\frac{\Delta H}{A}$, we can calculate by $\frac{\Delta H}{A} = \sigma + \frac{T \cdot \Delta S}{A}$.

3. The derivative of $T - \sigma$ relation

In this method, we also need to calculate σ of the studied liquid at different temperatures firstly, and then we can get an equation to describe the relationship between σ and T, i.e. $\sigma(T)$. After that the excess surface entropy can be easily calculated by $\frac{\Delta S(T)}{A} = \frac{-d\sigma(T)}{dT}$. And similarly, $\frac{\Delta H}{A} = \sigma + \frac{T \cdot \Delta S}{A}$.

Reference:

Dutcher, C. S., Wexler, A. S., and Clegg, S. L.: Surface tensions of inorganic multicomponent aqueous electrolyte solutions and melts, J Phys Chem A., 114, 12216-12230, 2010.
Sega, M., Horvai, G., and Jedlovszky, P.: On the calculation of the surface entropy in computer simulation. J. Mol. Liq., 262, 58-62, 2018.

Response to Comments from anonymous referee #1

General comments

1. In section 2.1, the authors note how simulations from 1000 K to 1700 K are used and extrapolated down to 298.15K. Is this a requirement from the simulation over simulations at lower temperatures? It is not clear whether any extrapolation would need to account for specific non-linearities that change over such a large temperature range. One might imagine any error in this process might impact on the offset presented in figure 3a?

Response:

Thanks to the reviewer for raising this important concern. A direct simulation of surface tension of molten NaCl at 298.15 K would not be possible, due to excessively large relaxation times of this system at this temperature (i.e., quick ions crystallization happens during simulation). It has been found that surface tensions of a very wide range of molten salts and their mixtures are well described by linear functions of temperatures over a temperature range of hundreds of degrees above the melting point (Horvath 1985, Janz 1988). Sada et al. (1984) also found for several molten salt hydrates that this linear relationship also applies to at least 5-10 ℃ below the melting point, without any discontinuity or change of slope. Thus, in the absence of simulation data of molten NaCl at very high degrees of supercooling (e.g., close or at room temperature), we follow the approach of Dutcher et al. (2010) and assume a linear relationship between surface tension of molten NaCl and temperature. With this approach, we could then retrieve the surface tension of molten NaCl at 298.15 K by extrapolating the simulated surface tension of molten NaCl in the temperature range of 1000 K to 1700 K, as shown in Fig. 5a. However, we agree with the reviewer that, in principle, non-linearity could still be possible at very high degrees of supercooling for the molten salts, which may introduce uncertainties to the offset obtained by the extrapolation. But to the best of our knowledge, no related study has been reported so far.

To clarify, we modified the related part in section 2.1 of the revised manuscript as "" following sentences "According to Dutcher et al. (2010), surface tension of liquid/molten NaCl at 298.15 K (corresponding x_{NaCl} is 1, infinite concentrated solution) can be regarded as the upper boundary of $\sigma_{NaCl,sol}$. *However, a direct simulation of surface tension of molten NaCl at 298.15 K would not be possible, due to excessively large relaxation times of this system at this temperature. It has been found that surface tensions of a very wide range of molten salts can be well described by linear functions of temperature (Sada et al., 1984; Horvath, 1985; Janz 1988; Dutcher et al., 2010). We thus follow the approach of Dutcher et al. (2010) assuming a linear relationship between surface tension of molten NaCl and temperature. With this approach, we retrieve the surface tension of molten NaCl at 298.15 K by extrapolating the simulated surface tension of molten NaCl in the temperature range of 1000 K to 1700 K. Note that, in principle, non-linearity could still be possible at very high degrees of supercooling (e.g., close to or at room temperature) for the molten salts, which may introduce uncertainties to the offset obtained by the extrapolation.* (Page 3, line 29-38)"

2. It would be nice to see some quantitative analysis of potential impact of this work. Whilst the impact of cloud activation processes should be small, where do the authors suggest this new dependency needs to be taken into account? For example given the below cloud focus, would it potentially influence the efflorescence transition RH according to the energy differential between a solid and saturated state? Would it affect growth rates in varying humidity environments? Could you perform some quantitative analysis on this? If not, please make it clear why.

Response:

Many thanks for the constructive comment. The reviewer is right, cloud activation processes are mainly related to the thermodynamic properties of diluted solutions. The thermodynamic properties, such as surface tension and water activity, for highly concentrated solution and for solute at molten state are essential for understanding the phase transition of nano particles (Cheng et al., 2015 and references therein). However, these data are difficult or even not possible to obtain due to technical difficulties. Although a transition regime ("plateau") around the concentration upon efflorescence (Fig. 4) was found, our simulation results in principle confirm the basic concept of the Dutcher et al. (2010) semi-empirical model. The MD simulations rather unfold a more detailed global landscape of concentration dependence of surface tension of aqueous NaCl solution, i.e., three regimes (a water-dominated regime, a transition regime and a molten NaCl-dominated regime) and their different driving forces, which may advance our understanding on the experiment-based findings that linear relationships between surface tensions of single inorganic electrolyte solutions may not valid for most highly soluble electrolytes (Dutcher et al., 2010). For example, surface tension of aqueous HNO_3 at ~298.15 K are linear only to mass fraction of HNO_3 ~0.2 (Weissenborn and Pugh, 1996); a clear plateau was found for the surface tension of aqueous ammonium sulfate (AS) at mass fraction of AS ~0.8 (the concentration upon efflorescence) (Cheng et al., 2015); and surface tension of aqueous NaCl clearly deviates from the linear function at molality of ~10 mol kg^{-1} (Cheng et al., 2015), which is consistent with the starting concentration point of the "plateau" (Fig. 4). Our result may not exactly reflect the real mode of surface tension of NaCl solution along the concentration, but it does imply the concept of a non-monotonic change of surface tension.

Following the suggestion, we also tried to evaluate the impact of the "plateau" on the estimation of vapor pressure upon gas-particle equilibrium with Köhler theory that accounts for the Kelvin effect. According to the MD simulation, the surface tension of aqueous NaCl upon efflorescence (x_{NaCl} of ~0.47) calculated by the E-AIM model should lower by ~5-6% (from ~ 93.2 mN/m to ~87.7 mN/m). For NaCl particles with diameter larger than 10 nm, the discrepancy in the vapor pressure estimations at x_{NaCl} of ~0.47 would be less than 1%, however, for smaller nano particles, it will lead to an underestimation of vapor pressure up to ~10% (for NaCl particles with diameter of ~ 1nm).

3. How applicable would the model be to other salts, particularly mixed salts that might arise in non-marine environments? The increased interest in bulk to surface partitioning studies require more thorough supporting studies on systems with surfactant organics. Where do MD simulations have a role here? Please guide the reader on some broad issues as to where you might demonstrate these tools in more obviously pressing issues.

Response:
Many thanks for the constructive comment. Our simulation approach can be used to study other salts, mixed salts and surfactant organics, when appropriate parameters are available, i.e. force fields that describe the interactions between salts and water, and the interactions between different individual slats. Here, we compared the values of surface tension of many organic compounds from MD simulations based on OPLS-AA force field and measured values to show the ability of MD simulations (Caleman et al., 2011). In Figure R3, calculated values are plotted against the measured values, and all data points compactly located around the 1:1 line with slight tendency of underestimation, which suggests that MD simulations can predict the measured values reasonably well.

Although our simulation approach can be used to study other systems, we cannot conclude if the non-monotonic change of surface tension along concentration also applies to other salts or mixed system and surfactant organics. It is worth to notice that, although surface tensions of single inorganic electrolyte solutions are often assumed to be linear functions of concentration or molality over moderate concentration range, this linear relation may not be valid for most highly soluble electrolytes (Dutcher et al., 2010). For example, surface tension of aqueous HNO_3 at ~298.15 K is linear only to mass fraction of HNO_3 ~0.2 (Weissenborn and Pugh, 1996). In our previous study (Cheng et al., 2015), surface tensions of NaCl solution and ammonium sulfate solution were studied by using Differential Köhler Analysis. Anomaly was found on the surface tension-molality curve for both salts. Our result may not exactly reflect the real mode of surface tension of NaCl solution along the concentration, but it does imply the concept of a non-monotonic change of surface tension. Therefore, we think more studies are necessary to examine the concentration dependence of surface tension of other salts or mixed system and surfactant organics by using MD simulations.

To emphasize, we add the following sentences into the conclusion: "…*One must be aware that for nucleation processes in the atmosphere also other chemical compounds matter, and will require future study. Also, mixed salt solutions would be very interesting, and can in principle be studied with similar simulation methods as applied here; however, this task must be left to future work.* (Page 8, line 30-33)".

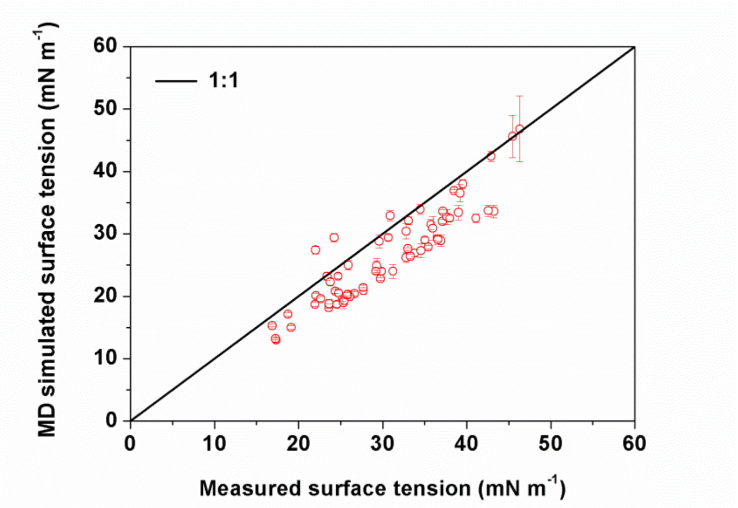

Figure R3. Correlation between calculated surface tension and measured values. All data used in Figure R3 is also summarized in Table R3. Data source: Caleman et al. (2011).

Table R3. Surface tension of 67 organic compounds from measurements and MD simulations. Data source: Caleman et al. (2011).

No.	Name	Measured Values	Calculated Values	No.	Name	Measured Values	Calculated Values
1	methanoic acid	37.13	32±0.4	35	pentane-2,4-dione	30.9	32.9±0.9
2	nitromethane	36.53	29.2±0.4	36	methyl 2-methylprop-2-enoate	24.24	29.4±0.7
3	methanol	22.07	20.1±0.4	37	ethyl propanoate	23.8	22.3±0.5
4	1,2-dibromoethane	39.55	38±0.7	38	diethyl carbonate	25.92	25±0.8
5	methylformate	24.36	20.8±0.3	39	pentan-1-ol	25.36	19±1
6	bromoethane	23.62	18.2±0.6	40	pentan-3-ol	23.65	18.8±0.7
7	N-methylformamide	38.52	36.9±0.2	41	pentane-1,5-diol	46.32	46.8±5.3
8	ethanol	21.97	18.7±0.3	42	nitrobenzene	43.23	33.6±1
9	methylsulfinylmethane	42.92	42.4±0.9	43	2-methylpyridine	33	27.6±0.2
10	ethane-1,2-diamine	41.12	32.5±0.7	44	3-methylpyridine	35.04	29±0.5
11	prop-2-enenitrile	26.63	20.4±0.3	45	4-methylpyridine	35.43	27.9±0.3
12	1,2-dibromopropane	34.5	33.9±0.8	46	cyclohexanone	34.57	27.3±1.1
13	methylacetate	24.73	23.2±0.4	47	hexan-2-one	25.45	19.3±0.6
14	1-bromopropane	25.26	19.4±0.2	48	cyclohexanamine	31.22	24±1.1
15	N,N-dimethylformamide	35.74	31.5±0.8	49	2-propan-2-yloxypropane	17.27	13.2±0.2
16	1-nitropropane	29.85	24±0.5	50	1-methoxy-2-(2-methoxyethoxy)ethane	29.3	24.9±1.1
17	2-nitropropane	29.29	24.9±0.8	51	triethyl phosphate	29.61	28.8±1.1
18	dimethoxymethane	18.75	17.1±0.3	52	N-propan-2-ylpropan-2-amine	19.14	15±0.3
19	propan-2-amine	17.36	13±0.3	53	benzaldehyde	38	32.5±0.5
20	ethylsulfanylethane	24.57	18.7±0.5	54	toluene	27.73	20.9±0.5
21	butane-1-thiol	25.22	19.9±0.3	55	phenylmethanol	35.97	30.9±1.9
22	butane-1,4-diol	45.47	45.6±3.4	56	2,4-dimethylpentan-3-one	24.78	20.5±0.5
23	2-methylpropan-2-amine	16.87	15.3±0.2	57	heptan-2-one	26.12	19.9±0.2
24	furan	22.65	19.6±0.4	58	1-phenylethanone	39.04	33.4±1.2
25	thiophene	30.68	29.4±0.5	59	methyl benzoate	37.17	33.6±0.3
26	1H-pyrrole	36.95	28.9±0.9	60	methyl 2-hydroxybenzoate	39.22	36.5±1.4
27	ethenyl acetate	22.03	27.4±0.6	61	1,2-dimethylbenzene	29.76	22.8±0.2
28	ethyl acetate	23.39	23.2±0.6	62	1,2-dimethoxybenzene	32.8	30.4±1.2
29	thiolane	33.82	26.9±0.6	63	2,4,6-trimethylpyridine	33.3	26.4±0.4
30	1-bromobutane	25.9	20.3±0.6	64	quinoline	42.59	33.7±0.9
31	N,N-dimethylacetamide	33.09	32.1±0.6	65	(1-methylethyl)benzene	27.69	21.4±0.4
32	morpholine	37.68	32.7±1.2	66	1,2,4-trimethylbenzene	29.19	24±0.4
33	pyridine	36.56	29.1±0.8	67	2,6-dimethylheptan-4-one	25.8	20.2±0.4
34	cyclopentanone	32.8	26.2±0.8				

Minor comments:

1. Page 2, line 10: I would suggest - size-effects at ‘the’ nanoscale.

Response: Thanks. We have revised the manuscript accordingly. "…*Because of the energy barrier of crystallization during dehydration and size-effects at the nanoscale*… (Page 2, line 8 in the revised manuscript)".

2. Page 2, line 38: Suggest - based on the 'following' concept

Response: Thanks. We have revised the manuscript accordingly. "…*This model is based on the following concept*… (Page 2, line 36 in the revised manuscript)"

3. Page 2, line 40: "solute" (t)hat

Response: Thanks. We have revised the manuscript accordingly. "…*while at very high salt concentration the water is considered as "solute" that is solvated by the ions*… (Page 2, line 38 in the revised manuscript)"

Reference:

Caleman, C., van Maaren, P J, Hong M., Hub, Jochen S., da Costa, Luciano T., and van der Spoel, David.: Force field benchmark of organic liquids: density, enthalpy of vaporization, heat capacities, surface tension, isothermal compressibility, volumetric expansion coefficient, and dielectric constant, J Chem Theory Comput., 8(1), 61-74, 2011.

Cheng, Y., Su, H., Koop, T., Mikhailov, E., and Pöschl, U.: Size dependence of phase transitions in aerosol nanoparticles, Nat. Commun., 6, 5923, doi:10.1038/ncomms6923, 2015.

Dutcher, C. S., Wexler, A. S., and Clegg, S. L.: Surface tensions of inorganic multicomponent aqueous electrolyte solutions and melts, J Phys Chem A., 114, 12216-12230, 2010.

Horvath, A. L.: Handbook of aqueous electrolyte solutions physical properties, estimation and correlation methods; Ellis Horwood series in physical chemistry, Ellis Horwood Limited: New York, 1985.

Janz, G. J.: Thermodynamic and transport properties for molten salts: correlation equations for critically evaluated density, surface tension, electrical conductance, and viscosity data, Amer Inst of Phys., 17, 1-39, 1988.

Sada E., Katoh S., and Damle, H G.: Surface tension of some molten salt hydrates by the pendant drop technique, J Chem Eng Data., 29(2), 117-119, 1984.

Weissenborn, P K., and Pugh, R J.: Surface tension of aqueous solutions of electrolytes: relationship with ion hydration, oxygen solubility, and bubble coalescence. J. Colloid Interface Sci., 184(2), 550-563, 1996.

Response to Comments from anonymous referee #2

General comments

1. Can the authors comment further on other systems such as KCl, NH4Cl, NaNO3, and NH4NO3, at least qualitatively? What about mixed-salt systems? Are the same behaviors expected?

Response:

Many thanks for the constructive comment. As in our response to general comment 3 of reviewer #1, our simulation approach can be used to study other salts (such as KCl, NH_4Cl, $NaNO_3$, and NH_4NO_3), as well as mixed salts and organics, when appropriate parameters are available, i.e. force fields those describe the interactions between salts and water, and the interactions between different individual slats. However, we cannot conclude if the non-monotonic change of surface tension along concentration also applies to other salts or mixed system. It is worth to notice that, although surface tensions of single inorganic electrolyte solutions are often to be linear functions of concentration or molality over moderate concentration range, this linear may not valid for most highly soluble electrolytes (Dutcher et al., 2010). For example, surface tension of aqueous HNO_3 at ~298.15 K are linear only to mass fraction of HNO_3 ~0.2 (Weissenborn and Pugh, 1996). In our previous study (Cheng et al., 2015), surface tension of NaCl solution and ammonium sulfate solution were studied by using Differential Köhler Analysis. Anomaly was also found on the surface tension-molality curve for both salts. Our result may not exactly reflect the real mode of surface tension of NaCl solution along the concentration, but it does imply the concept of a non-monotonic change of surface tension. Therefore, we think more studies are necessary to examine the concentration dependence of surface tension of other salts or mixed system and surfactant organics by using MD simulations.

To emphasis, we add the following sentences into the conclusion: "…*One must be aware that for nucleation processes in the atmosphere also other chemical compounds matter, and will require future study. Also, mixed salt solutions would be very interesting, and can in principle be studied with similar simulation methods as applied here; however, this task must be left to future work.* (Page 8, line 30-33)"

2. In the transition regime, is there any reason entropy is increasing as the mass fraction approaches the efflorescence point?

Response:

Many thanks for the constructive comment. We sincerely apologize that during the revision of the manuscript, we discovered an error in the submitted manuscript when using the pressure tensor method to calculate surface tension (please find more details in the Technical correction in the letter to the editor). Although our major finding and conclusions remain unaffected, the mis-calculation propagates the error into the energetic analyses and leads to the moderate increase of surface entropy in the transition regime when the solution concentration approaches the efflorescence point (Fig. R3b, Fig. 6 in the previously submitted manuscript). After re-simulating all cases and correcting the calculation of surface tension, we found that the surface entropy keeps almost unchanged, as shown in Fig. R3a (Fig. 6 in the revised manuscript and the related discussion has also been modified accordingly). We speculate this stability of surface entropy may be related to the surface enrichment zone of ions. Thus, the following sentences were added: "*Tentatively, one may correlate the formation of the enrichment zone with the stability of the surface entropy in this region via the entropy of mixing. At the same time, the surface enhancement of ions may be related to the phenomenon of efflorescence.* (Page 8, line 9-11)".

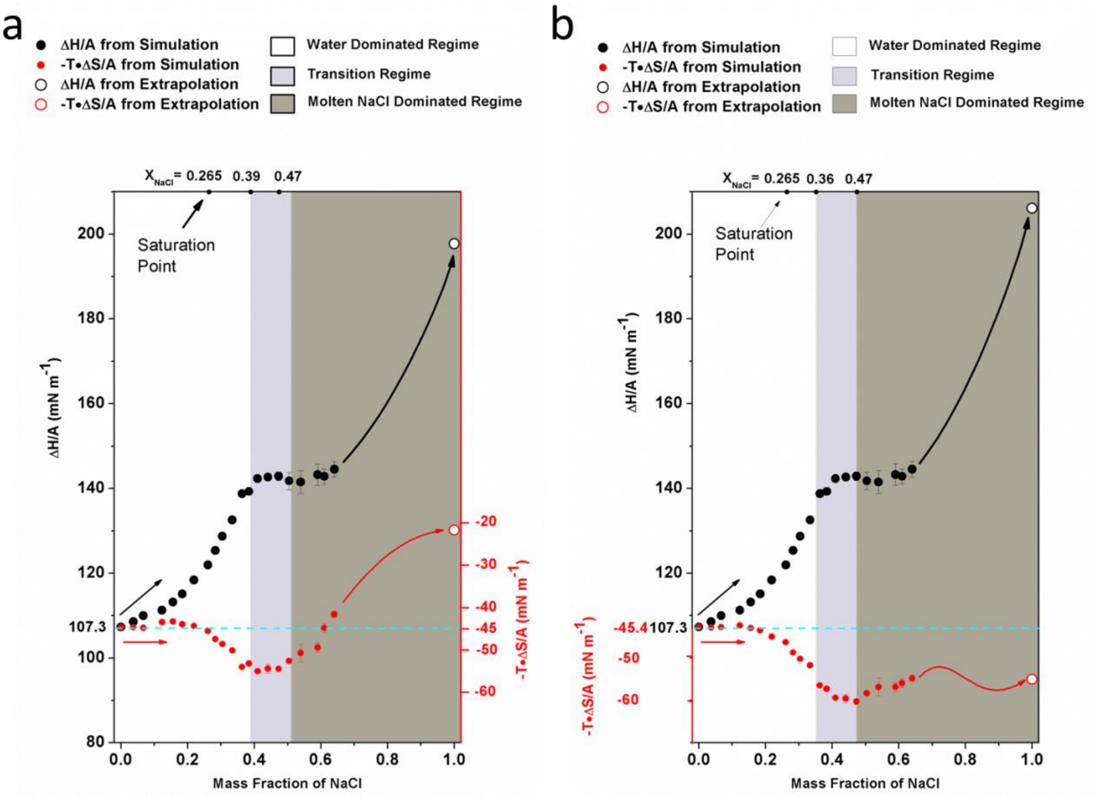

Figure R3. The excess surface enthalpy and entropy per unit area ($\frac{\Delta H}{A}$ and $\frac{T\cdot\Delta S}{A}$) of different NaCl solution concentrations. (a) the corrected Figure 6 in the revised manuscript. (b) the original Figure 6 in the submitted manuscript. $\frac{\Delta H}{A}$ (black circles) and $-\frac{T\cdot\Delta S}{A}$ (red circles) are shown as a function of mass fraction of NaCl. The solid circles are obtained from simulation directly, and the open circles are obtained from the extrapolation of corresponding properties of molten NaCl. The cyan dashed line is only an auxiliary line for clearer view.

Reference:

Cheng, Y., Su, H., Koop, T., Mikhailov, E., and Pöschl, U.: Size dependence of phase transitions in aerosol nanoparticles, Nat. Commun., 6, 5923, doi:10.1038/ncomms6923, 2015.

Weissenborn, P K., and Pugh, R J.: Surface tension of aqueous solutions of electrolytes: relationship with ion hydration, oxygen solubility, and bubble coalescence. J. Colloid Interface Sci., 184(2), 550-563, 1996.

Response to Interactive comment from W. R. Smith

On p. 4, line 15, 3 references are given for the solubility of the SPC/E-compatible NaCl force field of Joung and Cheatham (JC): The value is correctly given as 3.7±0.2. However, the first reference (Paluch et al, 2010) provides a result (which is incorrect) for a different force field. The paper of Aragones et al (2012) gives an incorrect result for the JC force field. The correct value of 3.7 ±0.2 is provided only in the final reference (Espinosa et al, 2016). The first two references should be omitted, since the first is irrelevant and the second gives an incorrect result. The history of the attempts to correctly calculate the aqueous solubility for the JC force field at 298.15K and 1 bar may be of interest. The correct value of 3.7±0.2 was first correctly calculated by my group: author = Moučka, F. and Nezbeda, I. and Smith, W. R., title = Molecular Force Field Development for Aqueous Electrolytes: 1. Incorporating Appropriate Experimental Data and the Inadequacy of Simple Electrolyte Force Fields Based on Lennard–Jones and Point Charge Interactions with Lorentz–Berthelot Rules, journal = J. Chem. Theory Comput., volume = 9, number = 11, pages = 5076-5085, year = 2013 Our result was later corroborated by the Panagiotopoulos group: author = Mester, Z. and Panagiotopoulos, A. Z., title = Mean ionic activity coefficients in aqueous NaCl solutions from molecular dynamics simulations, journal = J. Chem. Phys., volume = 142, number = 4, pages = 044507, year = 2015 and by Aragones et al. (2012) and Espinosa et al. (2016). The history of the attempts to correctly calculate the quantity by molecular simulation are described in the following review article: author = Nezbeda, I. and Mouˇcka, F. and Smith,W. R., title = Recent progress in molecular simulation of aqueous electrolytes: force fields, chemical potentials and solubility, journal = Molec. Phys., volume = 114, number = 11, pages = 1665-1690, year = 2016

Response:

We thank Dr. W. R. Smith for the interactive discussion and comments. Following the suggestion, we carefully explore the history of the attempts to correctly calculate the solubility of NaCl in water at 298.15 K (Nezbeda et al., 2016) and we agree that it is more appropriate to cite the paper by Moučka et al., (2013) here. We have modify the related statement accordingly as "…*The solubility at 298.15 K based on JC force field with SPC/E model has been determined as 3.7±0.2 mol* kg^{-1} *(Moučka et al., 2013; Mester and Panagiotopoulos, 2015; Espinosa et al., 2016), which to our best knowledge is the value most close one to the experimental value of solubility (~6.15 mol* kg^{-1}*). Therefore, this force field is appropriate to be used to study the concentration dependence of properties. More details about the history of the attempts to correctly calculate the quantity by molecular simulation can be found in Nezbeda et al.'s review (2016).* (Page 4, line 18-23)"

Reference:

Aragones, J., Sanz, E., and Vega, C.: Solubility of NaCl in water by molecular simulation revisited, J. Chem. Phys., 136, 244508, 2012.

Espinosa, J., Young, J., Jiang, H., Gupta, D., Vega, C., Sanz, E., Debenedetti, P., and Panagiotopoulos, A.: On the calculation of solubilities via direct coexistence simulations: Investigation of NaCl aqueous solutions and Lennard-Jones binary mixtures, J. Chem. Phys., 145, 154111, 2016.

Paluch, A. S., Jayaraman, S., Shah, J. K., and Maginn, E. J.: A method for computing the solubility limit of solids: application to sodium chloride in water and alcohols, J. Chem. Phys., 133, 124504, 2010.

Mester Z., and Panagiotopoulos A Z.: Mean ionic activity coefficients in aqueous NaCl solutions from molecular dynamics simulations, J. Chem. Phys., 142(4), 044507, 2015.

Moučka F., Nezbeda I., and Smith W R.: Molecular force field development for aqueous electrolytes: 1. Incorporating appropriate experimental data and the inadequacy of simple electrolyte force fields based on Lennard-Jones and point charge interactions with Lorentz–Berthelot rules, J. Chem. Theory. Comput., 9(11), 5076-5085, 2013.

Nezbeda I., Moučka F., and Smith W R.: Recent progress in molecular simulation of aqueous electrolytes: Force fields, chemical potentials and solubility, Mol. Phys., 114(11), 1665-1690, 2016.

Molecular Dynamics Simulation of the Surface Tension of Aqueous Sodium Chloride: from Dilute to Highly Supersaturated Solutions and Molten Salt

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Abstract. Sodium chloride (NaCl) is one of the key components of atmospheric aerosols. The surface tension of aqueous NaCl solution ($\sigma_{NaCl,sol}$) and its concentration dependence are essential to determine the equilibrium water vapor pressure of aqueous NaCl droplets. Supersaturated NaCl solution droplets are observed in laboratory experiments and under atmospheric conditions, but the experimental data for $\sigma_{NaCl,sol}$ are mostly limited up to sub-saturated solutions. In this study, the surface tension of aqueous NaCl is investigated by molecular dynamics (MD) simulations and pressure tensor method from dilute to highly supersaturated solutions. We show that the linear approximation of concentration dependence of $\sigma_{NaCl,sol}$ at molality scale can be extended to the supersaturated NaCl solution until a molality of ~10.7 mol kg^{-1} (i.e., solute mass fraction (x_{NaCl}) of ~0.39). Energetic analyses show that this monotonic increase of surface tension is driven by the increase of excess surface enthalpy (ΔH) as the solution becomes concentrated. After that, the simulated $\sigma_{NaCl,sol}$ remains almost unchanged until x_{NaCl} of ~0.47 (near the concentration upon efflorescence). The existence of the "inflection point" at x_{NaCl} of ~0.39 and the stable surface tension of x_{NaCl} between ~0.39 and ~0.47 can be attributed to the nearly unchanged excess surface entropy term ($\mathrm{T} \cdot \Delta\mathrm{S}$) and the excess surface enthalpy term (ΔH). After a "second inflection point" at x_{NaCl} of ~0.47, the simulated $\sigma_{NaCl,sol}$ gradually regains the growing momentum with a tendency to approach the surface tension of molten NaCl (~175.58 mN m^{-1} at 298.15 K, MD simulation based extrapolation). This fast increase of $\sigma_{NaCl,sol}$ at $x_{NaCl} > 0.47$ is a process driven by excess surface enthalpy and excess surface entropy. Our results reveal different regimes of concentration dependence of the surface tension of aqueous NaCl at 298.15 K: a water-dominated regime (x_{NaCl} from 0 to ~0.39), a transition regime (x_{NaCl} from ~0.39 to ~0.47) and a molten NaCl-dominated regime (x_{NaCl} from ~0.47 to 1).

1. Introduction

Sodium chloride (NaCl) is one of the most important components of atmospheric aerosol particles (Finlayson-Pitts, 2003; Lewis and Schwartz, 2004). The aqueous NaCl solution droplet could participate in many atmospheric processes, such as phase transition, cloud activation, ice crystallization, long-range transport and chemical aging (Martin, 2000; Finlayson-Pitts, 2003; Ghorai et al., 2014; Wagner et al., 2015; Chen et al., 2016). To better understand these processes, the concentration-dependent surface tension of aqueous NaCl solution ($\sigma_{NaCl,sol}$) is essential to determine the equilibrium between NaCl solution droplet and water vapor (Jarvis and Scheiman, 1968; Dutcher et al., 2010).

Below saturation point (~6.15 mol kg $^{-1}$), $\sigma_{NaCl,sol}$ shows a near linear dependence on molality (Jarvis and Scheiman, 1968; Johansson and Eriksson, 1974; Aveyard and Saleem, 1976; Weissenborn and Pugh, 1995; Matubayasi et al., 2001) with a slope of 1.73±0.17 (Pegram and Record, 2006, 2007). Because of the energy barrier of crystallization during dehydration and size-effects at the nanoscale (Martin, 2000; Biskos et al., 2006; Cheng et al., 2015), supersaturated aqueous NaCl solution droplets can exist under atmospheric conditions. However, direct measurements of surface tension of supersaturated droplets are challenging due to technical difficulties (Harkins and Brown, 1919; Vargaftik et al., 1983; Richardson and Snyder, 1994; Kumar, 2001). Only recently, Bzdek et al. (2016) overcame this limitation with an optical tweezer method and extend the concentration range to ~8 mol kg $^{-1}$, where the near linear relationship still holds (Bzdek et al., 2016).

It is a matter of debate to which extent the approximation of a near linear dependence of surface tensions on molality can still be used for NaCl droplets. Cheng et al. (2015) used the Differential Köhler Analyses (DKA) method to retrieve the surface tension of NaCl aqueous droplets, and revealed a large deviation from the near linear increase at molality of ~10 mol kg^{-1}. In literature, such deviation in concentrated solution has also been found for other compounds, such as HNO_3 (Weissenborn and Pugh, 1996) and it is believed to be typically true for most highly soluble electrolytes (Dutcher et al., 2010). The reason for such deviation remains unclear.

Several models about surface tension have been developed for highly concentrated solutions, e.g., Li and Lu (2001), Li et al. (1999), Levin and Flores-Mena (2001). Li and Lu (2001) developed a model based on the Gibbs dividing surface concept, where the adsorption and desorption rate constants, saturated surface excess, stoichiometric coefficient of ions and mean ionic activity coefficient are needed. For NaCl aqueous solution, this model is suitable for solution with concentration up to ~5.5 mol kg $^{-1}$. Li et al. (1999) uses Debye-Huckel parameter, osmotic coefficient and a proportionality constant from the fitting of measured values to calculate the surface tension, which covers the concentration until saturation point of bulk NaCl aqueous solutions. The remaining models are mostly only suitable for the dilute electrolyte solutions, such as the one proposed by Levin and Flores-Mena (2001). In their valid concentration range, these surface tension models produce linear or near linear concentration dependence of $\sigma_{NaCl,sol}$ that agrees well with currently available observations.

One surface tension model that is able to predict $\sigma_{NaCl,sol}$ in the whole concentration range from infinitely dilute (x_{NaCl} = 0) to highly supersaturated solution to molten salts (x_{NaCl} = 1) was proposed by Dutcher et al. (2010), which has been adopted into the widely used Extended Aerosol Inorganics Model (E-AIM) (Wexler and Clegg, 2002). This model is based on the following concept: ions are solvated by the water at low salt concentrations, which means that water molecules form hydration shells around the ions; while at very high salt concentration the water is considered as “solute” that is solvated by the ions, which means that ions forms shells around the water molecules (Dutcher et al., 2010). Accordingly, for a diluted solution, the surface tension of water dominates and the surface tension of the solution equals the surface tension of water adjusted by a term that is proportional to the solute concentration. For a highly supersaturated solution, a similar relationship can be applied with the surface tension of molten salt as governing element. Legitimately, the model is then constrained by the surface tensions of water and molten salt. The parameterization of this model is obtained by fitting the data of sub-saturated solutions. When the aqueous NaCl solution gets concentrated, this model shows a nonlinear monotonically increasing trend of $\sigma_{NaCl,sol}$ generally in good agreement with observations, but no "inflection point" was introduced. It should be noted that the surface tension as a function of mole fraction of NaCl according to the Dutcher et al. (2010) model is essentially a linear interpolation between the surface tensions of water and molten NaCl.

In this study, we applied molecular dynamics (MD) simulations and pressure tensor method to calculate the concentration dependence of $\sigma_{NaCl,sol}$ from infinitely dilute (x_{NaCl} = 0) to highly supersaturated solution to molten salt (x_{NaCl} = 1). The concentration dependence of $\sigma_{NaCl,sol}$ is divided into 3 regimes: a water-dominated regime, a transition regime and a molten NaCl-dominated regime. We compare our results with the Dutcher et al. (2010) model, and present the principal underlying physical chemistry (driving forces) behind the change of surface tension along concentration changes.

2. Methods

2.1 MD simulation

MD simulations were carried out with the GROMACS 5.1 package (Abraham et al., 2015). The Na^+ ions, Cl^- ions and water molecules were added into a cubic box (L = 5 nm) to imitate the NaCl solution. The concentrations of simulated solutions are summarized in Table 1. To simulate the surface tension of supersaturated NaCl aqueous solution, we make use of the time window in the MD simulations before the crystallization starts in the system. The highest x_{NaCl} we can reach is ~0.64 (the corresponding concentration is ~30.39 mol kg^{-1}), below which the simulated surface tensions in three independent runs stably converge after 50 to 100 ns (Fig. 1). For more concentrated solutions, stable convergence cannot be reached, as for example large fluctuations are shown in Fig. 1d at x_{NaCl} of 0.75.

According to Dutcher et al. (2010), surface tension of liquid/molten NaCl at 298.15 K (corresponding x_{NaCl} is 1, infinite concentrated solution) can be regarded as the upper boundary of $\sigma_{NaCl,sol}$. However, a direct simulation of surface tension of molten NaCl at 298.15 K would not be possible, due to excessively large relaxation times of this system at this temperature. It has been found that surface tensions of a very wide range of molten salts can be well described by linear functions of temperature (Sada et al., 1984; Horvath, 1985; Janz 1988; Dutcher et al., 2010). We thus follow the approach of Dutcher et al. (2010) assuming a linear relationship between surface tension of molten NaCl and temperature. With this approach, we retrieve the surface tension of molten NaCl at 298.15 K by extrapolating the simulated surface tension of molten NaCl in the temperature range of 1000 K to 1700 K. Note that, in principle, non-linearity could still be possible at very high degrees of supercooling (e.g., close to or at room temperature) for the molten salts, which may introduce uncertainties to the offset obtained by the extrapolation.

The procedure of simulation we followed is (Fig. 2): (1) systems were firstly energetically minimized by the steepest-descent method (Stillinger and Weber, 1985) (2) Solutions were equilibrated in the *NVT* ensemble and *NPT* ensemble (pressure = 1 bar) with periodic boundary conditions in three directions. The temperature was controlled by using the Nosé–Hoover thermostat (Nosé 1984; Hoover 1985). The box volume change due to the variation of density at different temperatures, and in our case the length of cubic box varied from 4.9 nm to 5.1 nm. (3) The box was elongated along the z-direction with L_z = 20 nm to create two interfacial regions. (4) The solution was equilibrated and simulated with the *NVT* ensemble in the rectangular parallelepiped box at the corresponding temperature. (5) Systems without surfaces were also simulated for further energy analysis, and the trajectories obtained from step 2 were simulated with *NPT* ensemble. (6) All simulations were carried out for at least 200 ns, which is much longer than that in previous studies (a few nanoseconds, Jungwirth and Tobias, 2000; Neyt et al., 2013) because the system that we were dealing with is much more concentrated. 1 fs time step was adopted and conformations for analysis were saved every 2 ps. Both electrostatic interactions and van der Waals interactions were calculated using the particle mesh Ewald (PME) algorithm, which has been proven to be a good choice for accurate calculation of long-range interactions (Essmann et al., 1995; Fischer et al., 2015). To test the reproducibility, all the systems were simulated 3 times, and the respective statistical error bars were provided.

In our simulation, the Joung-Cheatham (JC) force field for NaCl (Joung and Cheatham III, 2009) with SPC/E water model (Berendsen et al., 1987) was applied to simulate the NaCl solution and molten NaCl. The solubility at 298.15 K based on JC force field with SPC/E model has been determined as 3.7±0.2 mol kg^{-1} (Moučka et al., 2013; Mester and Panagiotopoulos, 2015; Espinosa et al., 2016), which to our best knowledge is the value most close one to the experimental value of solubility (~6.15 mol kg^{-1}). Therefore, this force field is appropriate to be used to study the concentration dependence of properties. More details about the history of the attempts to correctly calculate the quantity by molecular simulation can be found in Nezbeda et al.'s review (2016).

2.2 Calculation of Surface Tension

Based on results from MD simulations, the surface tension was calculated by using the mechanical definition of the atomic pressure (Alejandre et al., 1995):

$$\sigma_{MD} = 0.5L_z[\langle P_{zz}\rangle - 0.5(\langle P_{xx}\rangle + \langle P_{yy}\rangle)] \quad (1)$$

where σ_{MD} can represent the surface tension of molten NaCl (σ_{NaCl}), NaCl solution ($\sigma_{NaCl,sol}$) or pure water (σ_{water}), L_z is the length of the simulation cell in the longest direction (along z-axis) and P_{aa} (a=x, y, z) denotes the diagonal component of the pressure tensor. The $\langle \dots \rangle$ refers to the time average. The factor 0.5 outside the squared brackets takes into account the two interfaces in the system. Only the stable values were taken as our calculated surface tension.

2.3 Energy analysis

The excess surface enthalpy denotes the additional enthalpy in the system due to the creation of surfaces. It can be calculated as the difference of enthalpy between solutions with and without surfaces (Bahadur et al., 2007),

$$\Delta \mathrm{H} = H_{b\_s} - H_b \quad (2)$$

where H_{b_s} is the total enthalpy of simulated systems with surfaces and H_b is the total enthalpy of simulated systems without surfaces. As the kinetic energy is the same for systems with or without surfaces and the difference of pV can be ignored, ΔH can be presented as

$$\Delta\mathrm{H} = E_{b\_s} - E_b \tag{3}$$

where E_{b_s} and E_b are the potential energy of the system with and without surfaces.

Then the surface tension can be determined by the excess surface free energy per unit area as in Eq. (4) (Davidchack and Laird, 2003):

$$\sigma = \frac{\Delta\mathrm{G}}{\mathrm{A}} = \frac{\Delta\mathrm{H} - \mathrm{T}\cdot\Delta\mathrm{S}}{\mathrm{A}} \tag{4}$$

where ΔG is the increased part of free energy due to the creation of surfaces, A is the total area of the surface we created, so $A = 2 \times a$ and a is the area of each created surface. ΔS is the excess surface entropy. We then can retrieve ΔS by using the data of enthalpy and surface tension:

$$\Delta\mathrm{S} = \frac{\Delta H - \sigma \cdot A}{T} \tag{5}$$

ΔH and $\mathrm{T} \cdot \Delta\mathrm{S}$ per unit area ($\frac{\Delta\mathrm{H}}{\mathrm{A}}$ and $\frac{\mathrm{T}\cdot\Delta\mathrm{S}}{\mathrm{A}}$) are obtained as the enthalpic and entropic part of contributions to the net surface tension, which will be used to explain the change of surface tension along with the mass fraction of NaCl (x_{NaCl}).

3. Results and Discussion

3.1 Water-dominated regime ($x_{NaCl} <$ ~0.39)

In Fig. 3a, the calculated surface tension of NaCl aqueous solution ($\sigma_{NaCl,sol}$) is compared with experimentally determined values (Jarvis and Scheiman, 1968; Johansson and Eriksson, 1974; Aveyard and Saleem, 1976; Weissenborn and Pugh, 1995; Matubayasi et al., 2001; Pegram and Record, 2006, 2007; Morris et al., 2015; Bzdek et al., 2016) in the sub-saturated concentration range (molality of NaCl solution from 0 to 6.15 mol kg^{-1} and x_{NaCl} from 0 to ~0.265). At 298.15 K, both model simulation (red solid points and fit line in Fig. 3a) and experimental observation (black line in Fig. 3a) reveal a linear dependence of surface tension on solution concentration at molality scale, with a very similar slope (2.1 versus 1.73±0.17, respectively). Systematic underestimation, however, exists in the simulated $\sigma_{NaCl,sol}$. The previous MD simulations by Neyt et al. (2013) has also reported a similar result for the solution whose concentration ranges from 0 to 5.2 mol kg $^{-1}$ by using the same water model (SPC/E) but two different NaCl force fields, i.e., Wheeler NaCl (solid dark blue triangle in Fig. 3a) and Relf NaCl (open light blue triangle in Fig. 3a). Bhatt et al. (2004) also used the Wheeler NaCl model and SPC/E water model revealing a linear dependence and underestimation. We also subtracted the experimentally determined and the MD simulated surface tension of pure water (σ_{water}) from the observed and modeled $\sigma_{NaCl,sol}$, respectively. The relative increase of surface tension ($\Delta\sigma = \sigma_{NaCl,sol} - \sigma_{water}$) from models and experiments converge nicely (Fig. 3b), and the former is only a little higher than the latter. The MD simulation is able to reproduce the increment in the growth of surface tension from pure water due to the addition of solute NaCl though the predicted absolute value of $\sigma_{NaCl,sol}$ is systematically underestimated, which may mainly be attributed to the discrepancy between observed σ_{water} and the modeled ones from the SPE/C water model.

By performing MD simulations in the supersaturated concentration range, we found that this linear relationship still holds beyond the saturation point until x_{NaCl} of ~0.39 (Fig. 4). As mentioned above, the laboratory experiments with elevated NaCl aqueous droplet and the optical tweezer method show that the linear relationship between $\sigma_{NaCl,sol}$ and NaCl concentration (molality scale) can be extended to ~8 mol kg^{-1} (Fig. 3) (Bzdek et al., 2016), corresponding to x_{NaCl} of ~0.33 (Fig. 4), which is consistent with our simulations.

3.2 Transition regime (x_{NaCl} from ~0.39 to ~0.47)

It was often found that surface tensions of single inorganic electrolyte aqueous solution were linear functions of concentration (at the molality scale) over moderate concentration range (Talbot, 1987; Dutcher et al., 2010). However, these simple relationships may not hold when the solutions become more concentrated. As shown in Fig. 4, starting from x_{NaCl} ~0.39, the simulated $\sigma_{NaCl,sol}$ remains almost unchanged until x_{NaCl} of ~0.47 (concentration upon efflorescence). This “inflection point” of $\sigma_{NaCl,sol}$ at x_{NaCl} of ~0.39 is supported by those determined by the DKA approach (Cheng et al., 2015), where a large deviation of surface tension from the monotonic linear increase. Note that beyond x_{NaCl} of ~0.47, the simulated surface tension increases again (Fig. 4). This “second inflection point”, right at the concentration upon efflorescence, may imply potential correlation with crystallization processes.

3.3 Molten NaCl-dominated regime (x_{NaCl} > ~0.47)

Beyond the “second inflection point” (x_{NaCl} > 0.47), the simulated $\sigma_{NaCl,sol}$ gradually increases more and more strongly (Fig. 4). Unfortunately, due to the large fluctuation in the surface tension simulation (Fig. 1), we are not able to extend our surface tension calculation in this way beyond x_{NaCl} of ~0.64. However, according to Dutcher et al. (2010), it is expected that the surface tension of the solution would ultimately approach the surface tension of the hypothetical molten solute (i.e., $x_{NaCl} = 1$) at the same temperature. This hypothesis has been found to be consistent with the DKA retrieval for a highly concentrated ammonium sulfate aqueous solution with molality of ~380 mol kg^{-1} (Cheng et al., 2015). We thus also try to constrain the growth of $\sigma_{NaCl,sol}$ by MD simulated surface tension of molten NaCl (σ_{NaCl}) at 298.15 K.

Similar to Janz (1988)’s experimental results, the simulated σ_{NaCl} is also linearly correlated with temperature from 1000 K (the simulated melting point of NaCl) to 1700 K, as shown in Fig. 5. Following Dutcher et al. (2010), a surface tension of ~175.58 mN m^{-1} is obtained for the hypothetical molten NaCl at 298.15 K by linear extrapolation of the MD simulated σ_{NaCl} at higher temperature, which is very close to the ~169.7 mN m^{-1} extrapolated from the experimental results (Dutcher et al., 2010). Combined with $\sigma_{NaCl} = \sigma_{NaCl,sol}(x_{NaCl} = 1) =$ ~175.58 mN m^{-1}, the simulated $\sigma_{NaCl,sol}$ in the concentration range of x_{NaCl} > 0.47 shows the tendency to ultimately approaching the surface tension of melting NaCl at 298.15 K, similar to the blue curve in Fig. 4 from the Dutcher et al. (2000) study.

3.4 Physical chemistry behind the regimes

In energetic analyses, surface tension was decomposed into excess surface enthalpy ($\frac{\Delta H}{A}$) and excess surface entropy ($\frac{T\cdot\Delta S}{A}$). Note that the increase in excess surface entropy ($\frac{T\cdot\Delta S}{A}$) or decrease of $-\frac{T\cdot\Delta S}{A}$ will contribute negatively to the growth of $\sigma_{NaCl,sol}$. The analyses show that the monotonic increase of surface tension in water-dominated concentration ranges (x_{NaCl} from 0 to ~0.39) is driven by the increase of $\frac{\Delta H}{A}$ when the solution becomes concentrated (Fig. 6). When the solution gets concentrated, $\frac{\Delta H}{A}$ first increases slightly with enhanced increasing rate at $x_{NaCl} >$~0.2 and in the supersaturated regime up to x_{NaCl} of ~0.39. $-\frac{T\cdot\Delta S}{A}$ behaves differently, it remains almost constant at about -45 mN m^{-1} first and only starts to decrease at x_{NaCl} ~0.2. This way, in this concentration range (x_{NaCl} from 0 to ~0.39), the increase of excess surface enthalpy outnumbers the increase of excess surface entropy and thus this physicochemical regime can be understood as an excess surface enthalpy-driving process.

The stable surface tension in the transition-regime concentration range (x_{NaCl} from ~0.39 to ~0.47) is attributed to that $-\frac{T\cdot\Delta S}{A}$ and $\frac{\Delta H}{A}$ are both almost unchanged. Figure 6 shows that in the concentration above x_{NaCl} of ~0.39, the increase of $\frac{\Delta H}{A}$ significantly slows down and stabilizes at ~145 mN m^{-1} when the mass fraction approaches the efflorescence point. During this period, $-\frac{T\cdot\Delta S}{A}$ keeps nearly unchanged, which results in a corresponding $\sigma_{NaCl,sol}$ almost independent to the solution concentration change.

Here, we present a potential explanation for the stability of surface tension in this region from the structural analysis. The ratio of Na$^+$ concentration at different positions to the average concentration of the whole system ($C_z/C_{average}$) in different solutions is shown in Fig. 7a. The three blue-toned lines represent the ratio of solution in the transition regime with x_{NaCl} from ~0.39 to ~0.47. All of them have apophysises (significant rise) near the surface and these apophysises almost overlap with each other. This phenomenon suggests that the solute in these solutions enriches close to the surface and the degree of enrichment is almost the same for the different-concentration solution. Here, we denote the significant difference of the solute concentration in bulk region and on surface as a type of liquid-liquid partitioning. To check if this partitioning is dependent on the size of solution slab, we calculate the corresponding value of a 3 nm × 3 nm × 10 nm solution slab with x_{NaCl} of 0.4 (Fig. 7b). There is still an apophysis near surface, thus we can claim that the partitioning is independent of the size of solution slab in the simulation. Note that this surface enrichment of NaCl does not mean that NaCl is enriched right on top of the solution surface. Actually the density profile of water extends about 0.2 nm beyond that of NaCl towards the vapor region. By contrast, the solution with x_{NaCl} >0.47 or <0.39 do not have this type of partitioning as shown by the red and green lines. This comparison implies that the stability of surface tension of solution with x_{NaCl} from ~0.39 to ~0.47 is related to the “bulk-surface” partitioning. This interpretation is only a conjecture, and more studies are needed to further examine this phenomenon and interpretation. The shallow minimum in the density profile for x_{NaCl} between 0.39 and 0.47 to the left of the maximum is somewhat unexpected, and one might expect equilibration problems. However, we have checked that this structural feature develops already during the first 10 ns of the MD simulation, and does not change at all during the residual 200 ns. Surface enrichment of NaCl can be expected, however, when the solubility limit of the water-rich solution in the bulk is reached. Very roughly, such phenomena are analogous to interfacial wetting phenomena such as surface melting of crystals (Frenken and Van der Veen, 1985), which sometimes is observed when the temperature is raised towards the triple point. In our case, the enrichment zone of NaCl (which is about

0.4 nm thick in Fig.7) would be a precursor effect to the (metastable) NaCl-rich bulk solution. Tentatively, one may correlate the formation of the enrichment zone with the stability of the surface entropy in this region via the entropy of mixing. At the same time, the surface enhancement of ions may be related to the phenomenon of efflorescence.

As shown in Fig. 6, when a solution gets more concentrated from x_{NaCl} of ~0.47 to ~0.64, the $\frac{\mathrm{\Delta H}}{\mathrm{A}}$ slightly increases from the plateau of ~145 mN m^{-1} but the change is only ~5 mN m^{-1}. The $-\frac{\mathrm{T\cdot\Delta S}}{\mathrm{A}}$ keeps increasing. So during this period, both surface excess enthalpy term and entropy term contribute to the growth of $\sigma_{NaCl,sol}$. To constrain the energetic analyses, the $\frac{\mathrm{T\cdot\Delta S}}{\mathrm{A}}$ and $\frac{\mathrm{\Delta H}}{\mathrm{A}}$ were also calculated for the molten NaCl at 298.15 K. According to Fig. 5, we have $\sigma_{\mathrm{NaCl}} = -0.0755 \cdot \mathrm{T} + 198.09$, then we can get $\frac{\Delta \mathrm{S_{NaCl}}}{\mathrm{A}}$ = 0.0755 mN m^{-1} K^{-1} because of $\frac{\Delta \mathrm{S(T)}}{\mathrm{A}} = \frac{-\mathrm{d}\sigma(\mathrm{T})}{\mathrm{dT}}$ (Landau and Lifshitz, 1969). Therefore, for molten NaCl ($\mathrm{x_{NaCl}} = 1.0$), $\frac{\mathrm{T\cdot\Delta S_{NaCl}}}{\mathrm{A}}$ at 298.16 K is 22.15 mN m^{-1}, and $\frac{\Delta \mathrm{H_{NaCl}}}{\mathrm{A}}$ at 298.15 K is 198.09 mN m^{-1} (Fig. 6). Here, we used the derivative of temperature-surface tension relation to calculate the excess surface entropy, and more discussions about the comparison of these methods can be found in the supplement (Fig. S1). According to Fig. 6, it is expected that excess surface enthalpy term will still have a large amount (about more than 50 mN m^{-1}) to grow until approaching $\frac{\mathrm{\Delta H}}{\mathrm{A}}$ of molten NaCl at 298.15 K. It is similar for surface excess entropy term while the increment is smaller. Thus, the fast increase in $\sigma_{NaCl,sol}$ in the concentration of x_{NaCl} from ~0.47 to 1 can be assumed to be a process driven by excess surface enthalpy and excess surface entropy.

4. Conclusion

The analysis based on the calculated surface tension confirms the basic concept of the Dutcher et al. (2010) semi-empirical model, while unfold a more detailed global landscape of concentration dependence of surface tension of aqueous NaCl solution and its driving forces: (1) a water-dominated regime (x_{NaCl} from 0 to ~0.39, at low concentrations ions are solvated by the water molecules, which means that water-structures/hydration shells are formed around ions); (2) a transition regime (x_{NaCl} from ~0.39 to ~0.47); and (3) a molten NaCl-dominated regime (x_{NaCl} from ~0.47 to 1, at very high salt concentration water molecules are solvated by the ions, which means that a salt-structure is formed around the water molecules). Note that our result may not exactly reflect the real mode of surface tension of NaCl solution along the concentration, but it does imply the concept of a non-monotonic change of surface tension. One must be aware that for nucleation processes in the atmosphere also other chemical compounds matter, and will require future study. Also, mixed salt solutions would be very interesting, and can in principle be studied with similar simulation methods as applied here; however, this task must be left to future work.

5. Data availability

Readers who are interested in the data should contact the authors: Yafang Cheng (yafang.cheng@mpic.de), Hang Su (h.su@mpic.de) or Xiaoxiang Wang (xiaoxiang.wang@mpic.de).

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Table 1. Concentrations of solution studied in our simulation and the calculated values of surface tension.

NO.	Number of water	Number of NaCl	Concentration (mol kg^{-1}) in bulk region [b]	x_{NaCl} in bulk region	Concentration (mol kg^{-1}) of whole solution	x_{NaCl} of whole solution	Surface tension (mN m^{-1})
1	4142	0	0	0	0	0	62.24±0.044
2	4058	42	0.657	0.037	0.575	0.0325	63.48±0.03
3	3976	83	1.235	0.067	1.159	0.0635	64.8±0.014
4	3824	159	2.41	0.123	2.309	0.119	67.41±0.089
5	3728	207	3.16	0.156	3.08	0.1528	69.49±0.006
6	3656	243	3.85	0.184	3.69	0.1776	70.76±0.1
7	3550	296	4.8	0.219	4.63	0.213	73.61±0.055
8	3452	345	6.04	0.261	5.552	0.245	76.06±0.14
9	3388	377	6.75	0.283	6.182	0.265	77.5±0.11
10	3314	414	7.47	0.304	6.94	0.288	79.7±0.19
11	3222	460	8.57	0.334	7.931	0.317	82.06±0.25
12	3108	517	9.745	0.36	9.24	0.351	84.35±0.143
13	3038	552	10.66	0.384	10.09	0.371	85.67±0.183
14	2960	591	11.83	0.409	11.09	0.3935	86.9±0.04
15	2868	637	13.49	0.44	12.339	0.419	87.83±0.25
16	2762	690	15.34	0.47	13.879	0.448	88.03±0.88
17	2636	753	17.37	0.504	15.87	0.481	88.77±0.42
18	2486	828	19.98	0.54	18.503	0.519	90.35±0.6
19	2368	887	24.6	0.59	20.81	0.549	93.4±2.157
20	2232	955	26.74	0.61	23.77	0.581	97.6±1.46
21	2122	1010	30.396	0.64	26.44	0.607	102.53±0.46
22[a]	2109	421	11.48	0.4018	11.09	0.3935	86.9±0.59

a. The solution slab in this system is 3 nm × 3 nm × 10 nm and the simulation box is 3 nm × 3 nm × 30 nm.

b. There is a little difference between the concentration in the bulk region and the one of the whole system due to surface effects. The values used in the main text are the ones in the bulk region

Figures

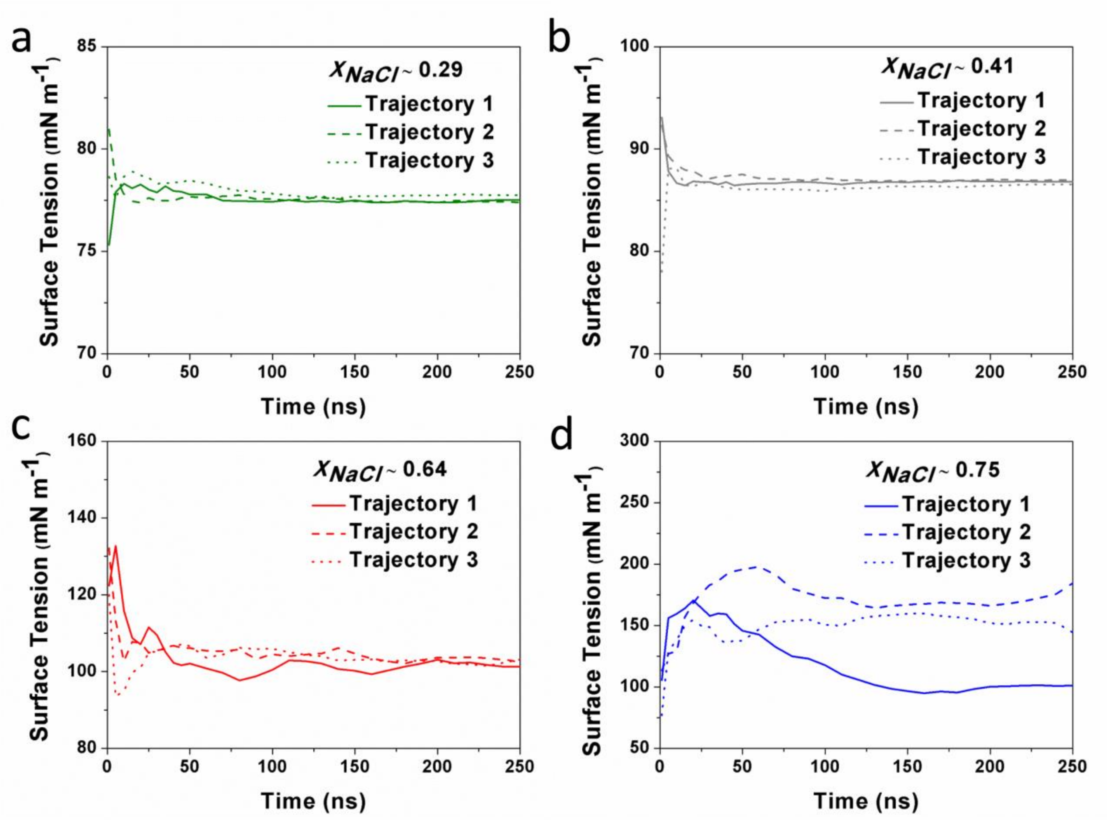

Figure 1. The calculated surface tension at different simulation time from different trajectories. For the solution with $x_{NaCl} \leq 0.64$ (a-c), the surface tension become steadily stabilized after ~100-150 ns, and different individual simulation runs converge to a similar result. When $x_{NaCl} > 0.64$ (d; here $x_{NaCl} = 0.75$), the surface tension keeps fluctuating and the final values from different individual simulations cannot be converged even after 250 ns.

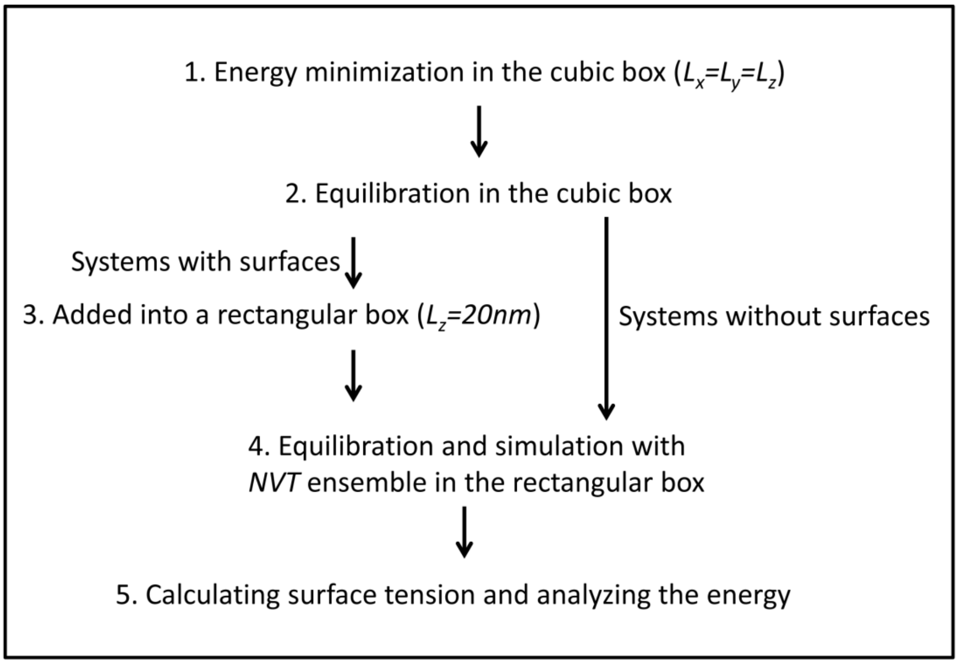

Figure 2. Schematic diagram of the different steps performed in the MD simulation.

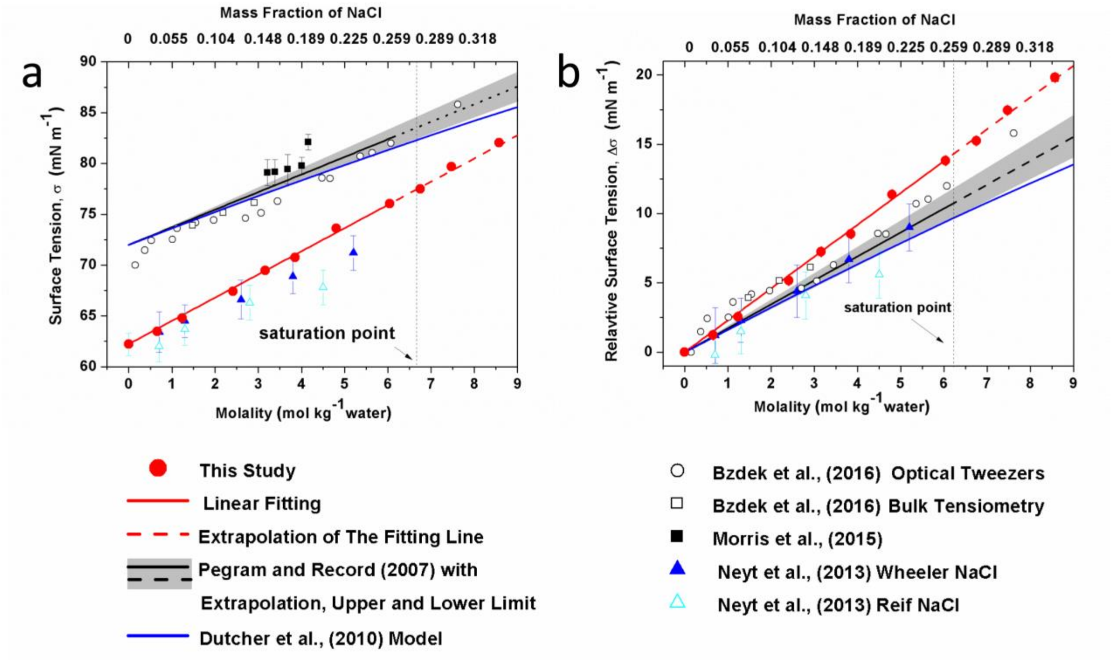

Figure 3. Surface tension (a) and relative surface tension (b) defined as $\Delta\sigma = \sigma_{solution} - \sigma_{water}$ as a function of the concentration of NaCl. The σ_{water} in the Morris et al. (2015) study was not determined, thus the corresponding Δσ is not shown in panel b.

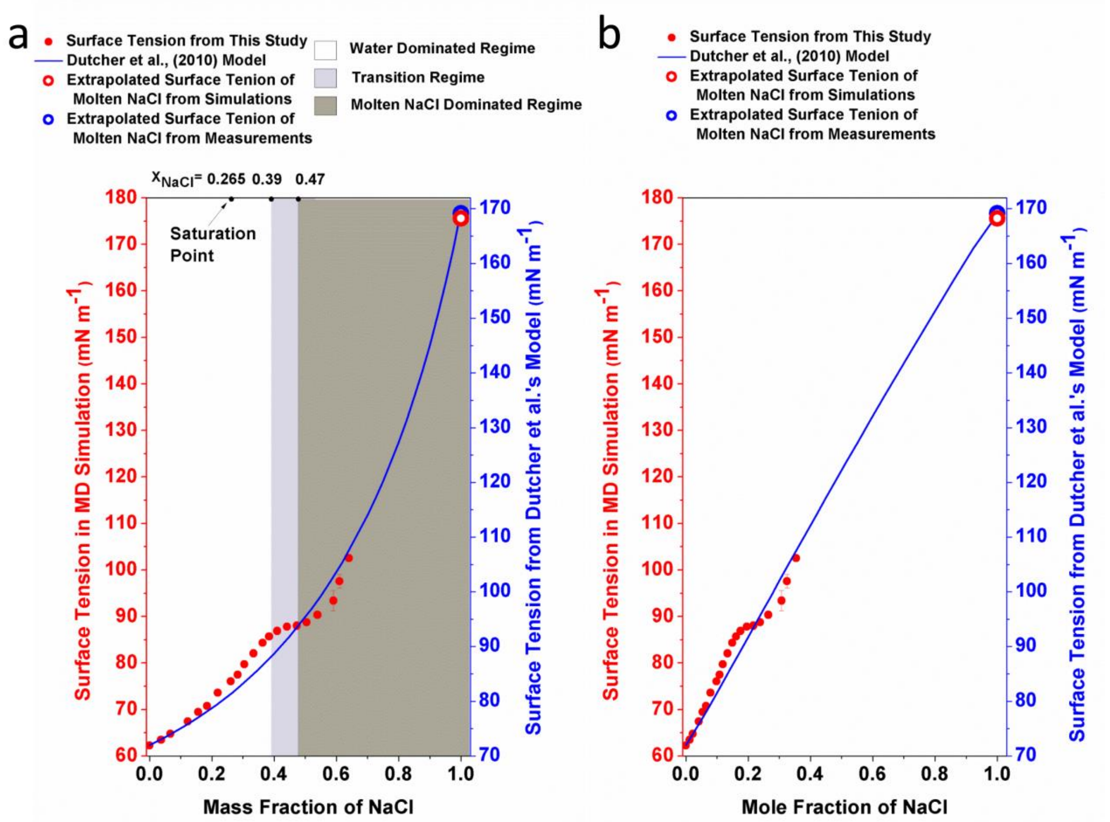

Figure 4. The surface tension of different-concentration NaCl solution. (a) The surface tension of NaCl solution against the mass fraction of NaCl. The left red y-axis is for the data from MD simulation (red circle), and the right blue y-axis is for the Dutcher et al. model (2010, blue solid line). The white, light grey and dark grey areas shade the water-dominated, transition and molten NaCl-dominated regimes, respectively. (b) The surface tension of NaCl solution is plotted against the mole fraction of NaCl.

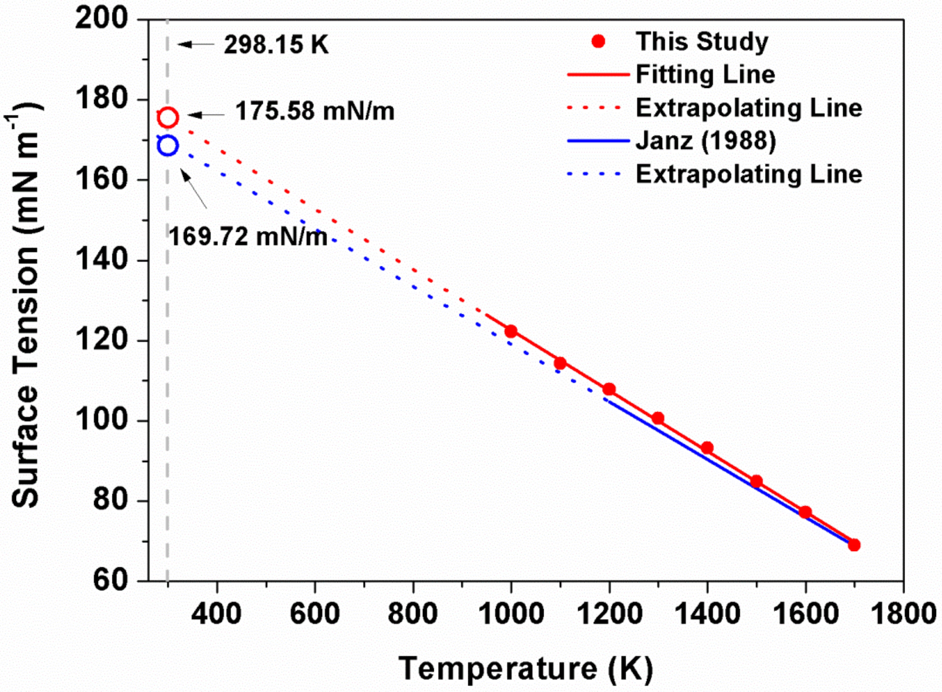

Figure 5. The surface tension of molten NaCl at different temperatures. The equation in Janz's study (1988) is $\sigma_{NaCl} = -0.07188 \cdot \mathrm{T} + 191$ (blue solid line). The fitting line based on our data is $\sigma_{NaCl} = -0.0755 \cdot \mathrm{T} + 198.09$ (red solid line). The red and blue open circles represent the extrapolated value of surface tension in simulation and reality.

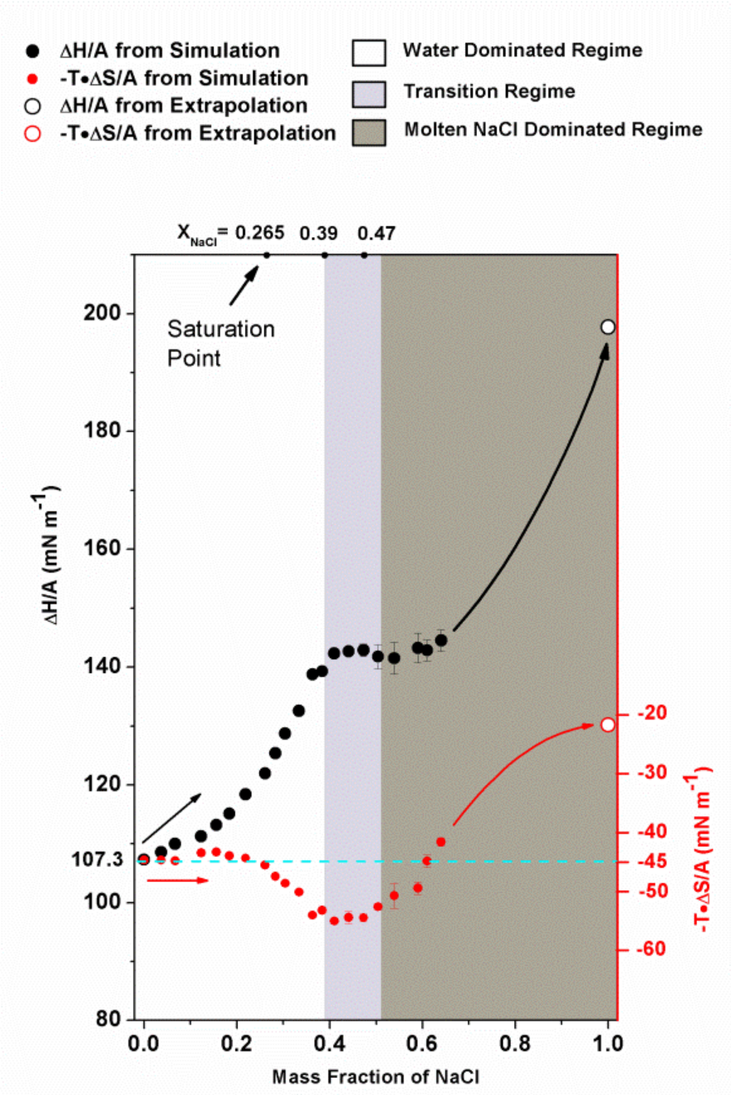

Figure 6. The excess surface enthalpy and entropy per unit area ($\frac{\Delta \mathrm{H}}{\mathrm{A}}$ and $\frac{\mathrm{T}\cdot\Delta \mathrm{S}}{\mathrm{A}}$) of different NaCl solution concentrations. $\frac{\Delta \mathrm{H}}{\mathrm{A}}$ (black circles) and $-\frac{\mathrm{T}\cdot\Delta \mathrm{S}}{\mathrm{A}}$ (red circles) are shown as a function of mass fraction of NaCl. The solid circles are obtained from simulation directly, and the open circles are obtained from the extrapolation of corresponding properties of molten NaCl. The cyan dashed line is only an auxiliary line for clearer view. Shaded areas are the same as in Figure 4.

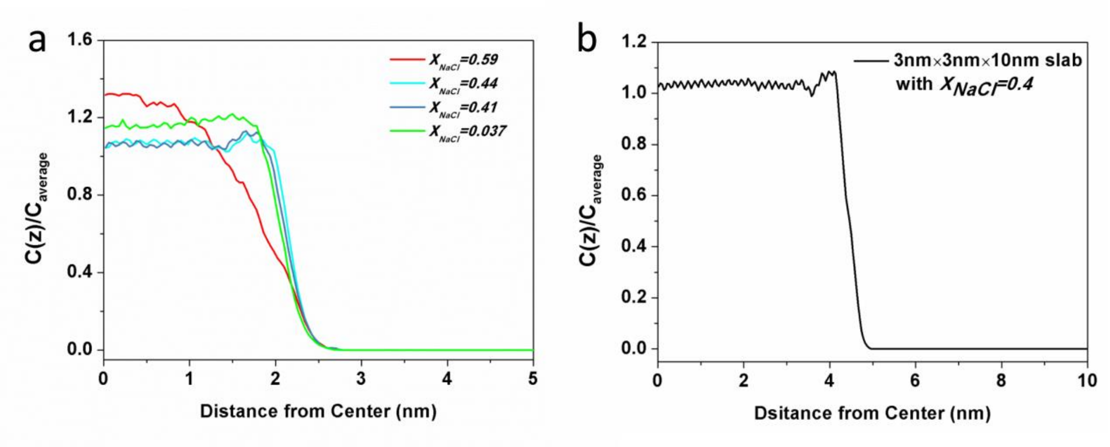

Figure 7. The ratio of Na$^+$ concentration at different positions (C_z) to the average concentration of the whole system ($C_{average}$). (a) The solution with x_{NaCl} = 0.59 (red line) is on behalf of the solution in the molten NaCl-dominated regime (red line), the solution x_{NaCl} = 0.44 and 0.41 (blue lines) represent the solution in transition regime, and the solution x_{NaCl} = 0.037 (green line) represents the solution in the water-dominated regime. (b) The density profile obtained from a 3 nm × 3 nm × 10 nm solution slab in which NaCl mass fraction is about 0.4.

Molecular Dynamics Simulation of the Surface Tension of Aqueous Sodium Chloride: from Dilute to Highly Supersaturated Solutions and Molten Salt

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Supplement

There are three ways to calculate the excess surface entropy, i.e. the direct method, the numerical derivative and the derivative of temperature-surface tension ($\mathrm{T}-\sigma$) relation (Sega and Dellago, 2017; Sega et al., 2018). The direct method was employed to calculate $\frac{\Delta\mathrm{H}}{\mathrm{A}}$ and $\frac{\mathrm{T}\cdot\Delta\mathrm{S}}{\mathrm{A}}$ in our paper (Fig. 6). In this method, we simulated liquid layers with and without surfaces. The difference of enthalpy per area of liquid with surfaces and the one of liquid without surfaces is the excess surface enthalpy ($\frac{\Delta\mathrm{H}}{\mathrm{A}}$). And $\frac{\mathrm{T}\cdot\Delta\mathrm{S}}{\mathrm{A}}$ can be calculated as $\frac{\mathrm{T}\cdot\Delta\mathrm{S}}{\mathrm{A}}=\frac{\Delta\mathrm{H}}{\mathrm{A}}-\sigma$. The numerical derivative method is based on the value of σ of the studied liquid at different temperatures. We need to use the equation $\sigma(\mathrm{T})=\sigma(\mathrm{T}_0)+\mathrm{a}\times(\mathrm{T}-\mathrm{T}_0)+\mathrm{b}\times(\mathrm{T}-\mathrm{T}_0)^2$ to fit the data of $\sigma(\mathrm{T}_0)$, $\sigma(\mathrm{T}_0-10\ \mathrm{K})$ and $\sigma(\mathrm{T}_0+10\ \mathrm{K})$ to get the fitting parameters a and b for a given T_0, i.e., $\mathrm{a}(\mathrm{T}_0)$ and $\mathrm{b}(\mathrm{T}_0)$, respectively. As $\frac{\Delta\mathrm{S}(\mathrm{T})}{\mathrm{A}}=\frac{-d\sigma(\mathrm{T})}{d\mathrm{T}}$ (Landau and Lifshitz, 1969), we have $\frac{\Delta\mathrm{S}}{\mathrm{A}}(\mathrm{T}_0)=-\mathrm{a}(\mathrm{T}_0)$. And we can get $\frac{\Delta\mathrm{S}}{\mathrm{A}}$ at different temperature one by one. For $\frac{\Delta\mathrm{H}}{\mathrm{A}}$, we can calculate by $\frac{\Delta\mathrm{H}}{\mathrm{A}}=\sigma+\frac{\mathrm{T}\cdot\Delta\mathrm{S}}{\mathrm{A}}$. The derivative of $\mathrm{T}-\sigma$ relation method is also based on the value of σ of at different temperatures. After obtaining these values, we can get an equation to describe the relationship between σ and T, i.e. $\sigma(\mathrm{T})$. After that the excess surface entropy can be easily calculated by $\frac{\Delta\mathrm{S}(\mathrm{T})}{\mathrm{A}}=\frac{-d\sigma(\mathrm{T})}{d\mathrm{T}}$ (Landau and Lifshitz, 1969). And similarly, $\frac{\Delta\mathrm{H}}{\mathrm{A}}=\sigma+\frac{\mathrm{T}\cdot\Delta\mathrm{S}}{\mathrm{A}}$.

A very recent paper (Sega et al., 2018) compared excess surface entropy based on these methods and reported that results based on the direct method might not be applicable at high temperature because of its significant deviations to the excess surface entropy derived with the derivative of $\mathrm{T}-\sigma$ relation when the temperature is high. Thus we used the derivative of $\mathrm{T}-\sigma$ relation method to calculate $\frac{\Delta\mathrm{H}}{\mathrm{A}}$ and $\frac{\mathrm{T}\cdot\Delta\mathrm{S}}{\mathrm{A}}$ of molten NaCl, but not the direct method. Note again that the majority of data in Fig. 6 (except the points for x_{NaCl} of 1.0) are obtained by the direct method at 298.15 K. We also performed independent calculation of the excess surface entropy and enthalpy of pure water at temperatures from 278.15 K to 348.15 K based on the aforementioned three methods. As shown in the Fig. S1, results from these three methods well agree with each other, which means that results based on the direct method at room temperature can be trusted.

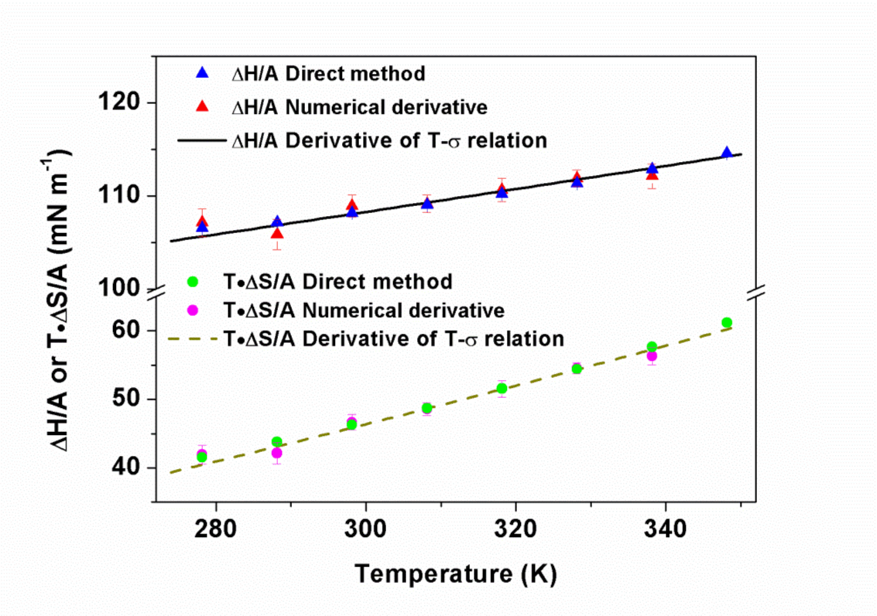

Figure S1. $\frac{\Delta \mathrm{H}}{\mathrm{A}}$ and $\frac{\mathrm{T}\cdot\Delta \mathrm{S}}{\mathrm{A}}$ of pure water at temperatures from 278.15 K to 348.15 K obtained from different methods.

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