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*Supplement of*

## **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 ( $T - \sigma$ ) relation (Sega and Dellago, 2017; Sega et al., 2018). The direct method was employed to calculate  $\frac{\Delta H}{A}$  and  $\frac{T \cdot \Delta S}{A}$  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 ( $\frac{\Delta H}{A}$ ). And  $\frac{T \cdot \Delta S}{A}$  can be calculated as  $\frac{T \cdot \Delta S}{A} = \frac{\Delta H}{A} - \sigma$ . The numerical derivative method is based on the value of  $\sigma$  of the studied liquid at different temperatures. We need to use the equation  $\sigma(T) = \sigma(T_0) + a \times (T - T_0) + b \times (T - T_0)^2$  to fit the data of  $\sigma(T_0)$ ,  $\sigma(T_0 - 10 \text{ K})$  and  $\sigma(T_0 + 10 \text{ K})$  to get the fitting parameters  $a$  and  $b$  for a given  $T_0$ , i.e.,  $a(T_0)$  and  $b(T_0)$ , respectively. As  $\frac{\Delta S(T)}{A} = \frac{-d\sigma(T)}{dT}$  (Landau and Lifshitz, 1969), 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  $\frac{\Delta H}{A} = \sigma + \frac{T \cdot \Delta S}{A}$ . The derivative of  $T - \sigma$  relation method is also based on the value of  $\sigma$  of at different temperatures. After obtaining these values, we can get an equation to describe the relationship between  $\sigma$  and  $T$ , i.e.  $\sigma(T)$ . After that the excess surface entropy can be easily calculated by  $\frac{\Delta S(T)}{A} = \frac{-d\sigma(T)}{dT}$  (Landau and Lifshitz, 1969). And similarly,  $\frac{\Delta H}{A} = \sigma + \frac{T \cdot \Delta S}{A}$ .

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  $T - \sigma$  relation when the temperature is high. Thus we used the derivative of  $T - \sigma$  relation method to calculate  $\frac{\Delta H}{A}$  and  $\frac{T \cdot \Delta S}{A}$  of molten NaCl, but not the direct method. Note again that the majority of data in Fig. 6 (except the points for  $x_{\text{NaCl}}$  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.

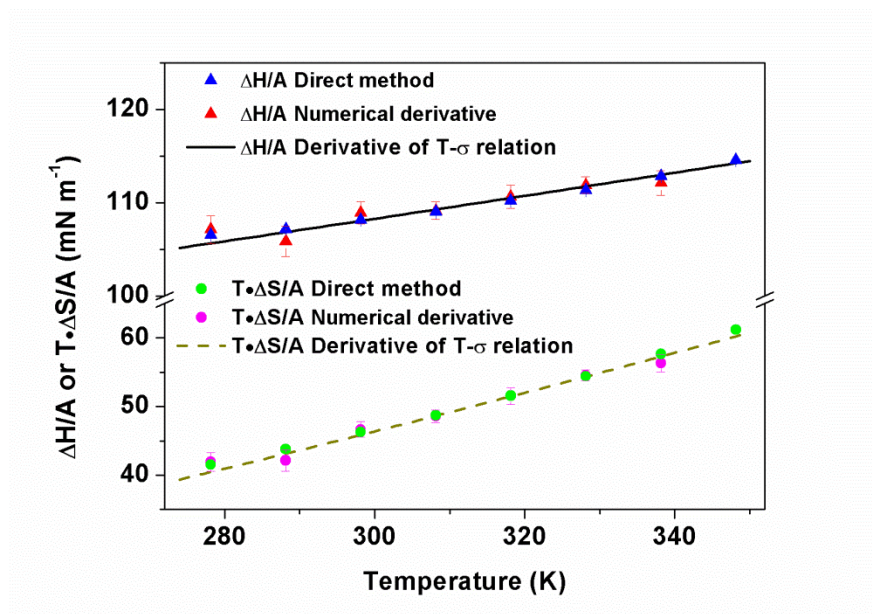


Figure S1.  $\frac{\Delta H}{A}$  and  $\frac{T \cdot \Delta S}{A}$  of pure water at temperatures from 278.15 K to 348.15 K obtained from different methods.

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