

Supporting information for the article titled  
"Using Grand Canonical Monte Carlo  
Simulations to Understand the Role of  
Interfacial Fluctuations on Solvation at the  
Water-Vapor Interface"

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1.  $\Delta\mu$  computed using the canonical ensemble simulations at  $T = 400$  K and 300 K.

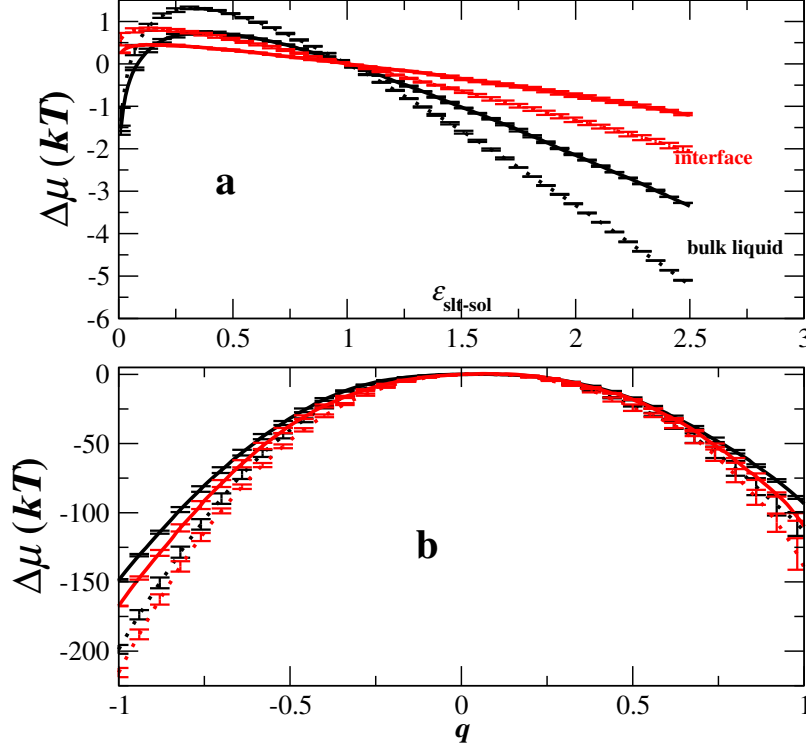


Figure S1: Relative solvation free energies in water for two positions of the solute at  $T = 400$  K and 300 K. The calculations are performed using the canonical EE simulations. The straight and dotted lines denote results obtained at 400 K and 300 K, respectively. (a) The variation of  $\Delta\mu$  with  $\epsilon_{\text{slt-sol}}$  ( $q = 0$ ). The values are plotted relative to  $\Delta\mu(\epsilon_{\text{slt-sol}} = 1.0)$ . (b) The variation of  $\Delta\mu$  with  $q$  ( $\epsilon_{\text{slt-sol}} = 1.0$ ). The values are plotted relative to  $\Delta\mu(q = 0.0)$ . Black and red lines denote the results for solute fixed in bulk liquid ( $z = 15$  Å) and near water-vapor interface ( $z = 29$  Å for  $T = 400$  K and  $z = 26.6$  Å for  $T = 300$  K), respectively. Uncertainties are shown at selected points.  $\Delta\mu$  is in units of  $kT$ .

2.  $\Delta\Delta\mu$  computed using the canonical ensemble simulations at  $T = 400$  K.

Figures S1 and S2 show the canonical ensemble results for  $T = 400$  K. Here,  $\Delta\Delta\mu$  is calculated by applying a field perpendicular to the liquid-vapor interface.<sup>1</sup> The interfacial fluc-

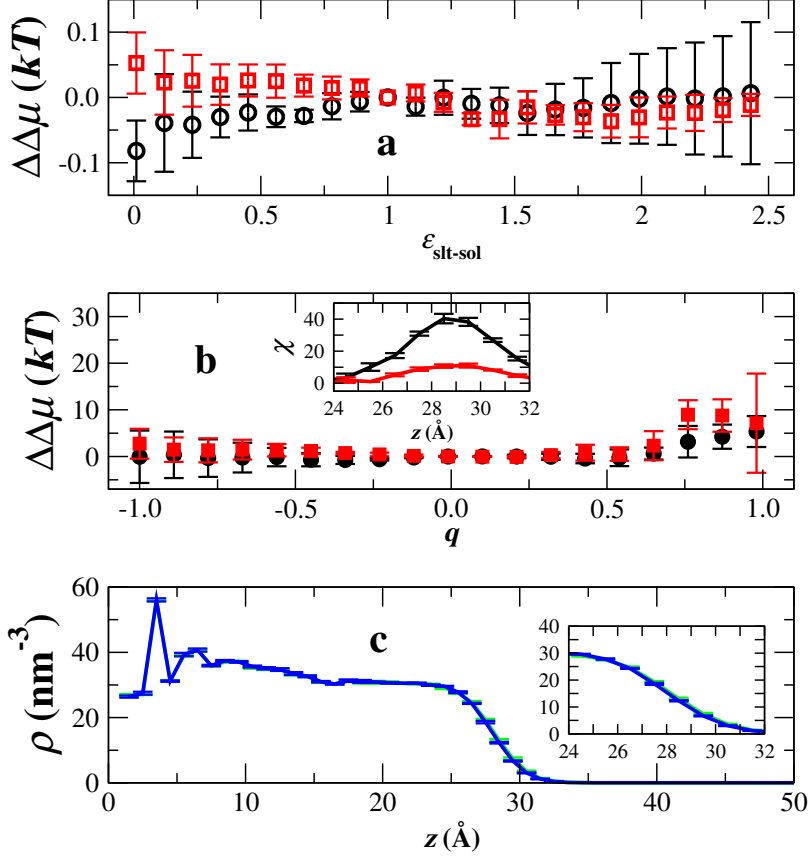


Figure S2: Change in solvation free energies in water due to the external field at  $T = 400$  K obtained from canonical EE simulations. The potential for the external field is given by the Equation (12) with  $\varepsilon_{\text{sw-field}} = 0.075kT$  and  $l_{\text{sw-field}} = 65.4$  Å. (a) The variation of  $\Delta\Delta\mu$  with  $\varepsilon_{\text{slt-sol}}$  ( $q = 0$ ). The values are plotted relative to  $\Delta\Delta\mu(\varepsilon_{\text{slt-sol}} = 1.0)$ . (b) The variation of  $\Delta\Delta\mu$  with  $q$  ( $\varepsilon_{\text{slt-sol}} = 1.0$ ). The values are plotted relative to  $\Delta\Delta\mu(q = 0.0)$ . The inset of "b" shows the local compressibility  $\chi$  as a function of  $z$ . Here, black and red straight lines denote results without and with field, respectively.  $\chi$  is plotted in units of  $\text{nm}^{-3}(kT)^{-1}$ . In Figures a and b, black and red symbols denote the results for solute fixed at  $z = 15$  Å (bulk liquid) and  $29$  Å (interface), respectively. Uncertainties are shown at selected points.  $\Delta\Delta\mu$  is in units of  $kT$  (c) Number density of oxygen sites of the water model. Green and blue straight lines denote the densities without and with the external field, respectively. The inset of c shows the magnified profile near liquid-vapor interface. Density is shown in the units of number of sites per  $\text{nm}^3$ .

tuations are substantially dampened by the applied field, as indicated by the drop in the maximum value of local compressibility  $\chi$  (The values of  $\chi$  were calculated using the procedure described in our earlier work<sup>1</sup>). The applied field does not affect the position of the liquid-vapor interface significantly, as seen from the density profiles. Therefore, it affects  $\Delta\mu$  predominantly via dampening of fluctuations. We observe that the magnitude of  $\Delta\Delta\mu$  for

the LJ solute is statistically insignificant over the entire range of  $\varepsilon_{\text{slt-sol}}$ , irrespective of its position. The same can be said about the ionic solute positioned in the bulk liquid. For the ionic solute at the interface, the magnitudes are statistically significant for strongly charged ions. Like the results from the grand canonical simulations, the above results indicate that the interfacial fluctuations play greater role in the variation of  $\Delta\mu$  with the strength of ion-water electrostatic interactions.

From Figures S1 and S2 it is possible to infer about the contribution of interfacial fluctuations to the free energy change  $\Delta\mu_{\text{ads}}$  associated with transferring a solute from bulk liquid to the interface. The difference between bulk and interfacial profiles for the ionic solute in Figure S1b denotes the net contribution of ion-water electrostatic interaction to  $\Delta\mu_{\text{ads}}$ . We observe that this magnitude can be as large as  $\approx 30kT$ . Coming to the role of fluctuations, let  $\Delta\Delta\mu_{\text{ads}}$  denote the difference between  $\Delta\mu_{\text{ads}}$  calculated with and without the external field in the canonical ensemble. It is then straightforward to show that

$$\Delta\Delta\mu_{\text{ads}} = \Delta\Delta\mu_{\text{int}} - \Delta\Delta\mu_{\text{bulk}} + \Delta\Delta\mu_{\text{int}}^{\text{ref}} - \Delta\Delta\mu_{\text{bulk}}^{\text{ref}} \quad (1)$$

Here, the sub-scripts bulk and int denote  $\Delta\Delta\mu$  for a solute positioned in bulk liquid and interface, respectively (Figure S2). The super-script ref denotes the corresponding values for the reference solute. In Figure S2 the reference is the LJ solute with the parameters same as the oxygen site of the SPC/E model. We have shown that the external field employed in the canonical ensemble simulations only dampens interfacial fluctuations. Therefore,  $\Delta\Delta\mu_{\text{ads}}$  can be interpreted as the effect of the above dampening on the free energy change of transferring the solute to the interface. Figure S2 shows that  $\Delta\Delta\mu_{\text{int}} - \Delta\Delta\mu_{\text{bulk}}$  for the ionic solute can be as large as  $5kT$ . The positive sign indicates that the electrostatic interaction between the ion and fluctuating water molecules at the interface favor the transfer of the solute towards the interface. Notice that this magnitude is small, but non-negligible as compared to the total contribution of solute-water electrostatic interaction to  $\Delta\mu_{\text{ads}}$  (approximately  $30kT$ ).

In the present document we do not discuss the sign of  $\Delta\Delta\mu$  because it is sensitive to

the position of solute with respect to the water-vapor interface. Therefore, whether the interfacial fluctuations favor or disfavor the solvation will depend on the position of the fixed solute with respect to water-vapor interface.

### 3. $\Delta\Delta\mu$ computed using the canonical ensemble simulations at $T = 300$ K.

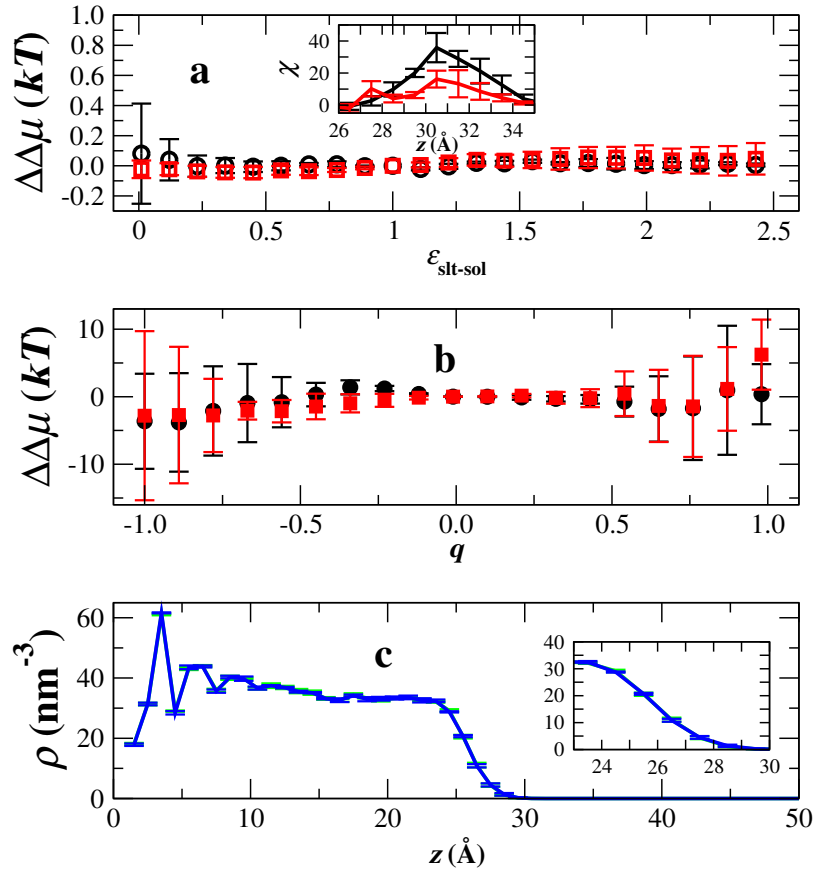


Figure S3: Change in solvation free energies in water due to the external field at  $T = 300$  K obtained using the canonical expanded ensemble (EE) simulations. The potential for the external field is given by the Equation (12) with  $\epsilon_{\text{sw-field}} = 0.1kT$  and  $l_{\text{sw-field}} = 65.4$  Å. In Figures a and b, black and red symbols denote the results for solute fixed at  $z = 15$  Å (bulk liquid) and  $26.6$  Å (interface), respectively. The inset of "a" shows the local compressibility  $\chi$  as a function of  $z$ . Rest of the details are same as in Figure S2.

Figures S1 and S3 show the results for  $\Delta\mu$  and  $\Delta\Delta\mu$  at 300 K. We only show results from

the canonical-ensemble-based calculations because of sampling difficulties in performing the GCEE simulations at this temperature. Also, note that the position of the liquid-vapor interface is slightly different than that for 400 K. Therefore, the position of the solute that is used for the interfacial calculations differs from the position used in the simulations at 400 K. This position was selected such that the density of surrounding water molecules is approximately same as that at 400 K. We observe that the trends in  $\Delta\mu$  are similar to those at 400 K. However, the magnitudes of  $\Delta\Delta\mu$  are insignificant for all the scenarios. Thus, the interfacial fluctuations appear to have a negligible effect on  $\Delta\mu$  over the investigated range of solute-solvent interactions.

## References

- (1) Rane, K.; van der Vegt, N. F. A. Understanding the influence of capillary waves on solvation at the liquid-vapor interface. *The Journal of Chemical Physics* **2016**, *144*, 114111.