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Supplementary information: On the microscopic origin of cryoprotective effect in lysine solutions†

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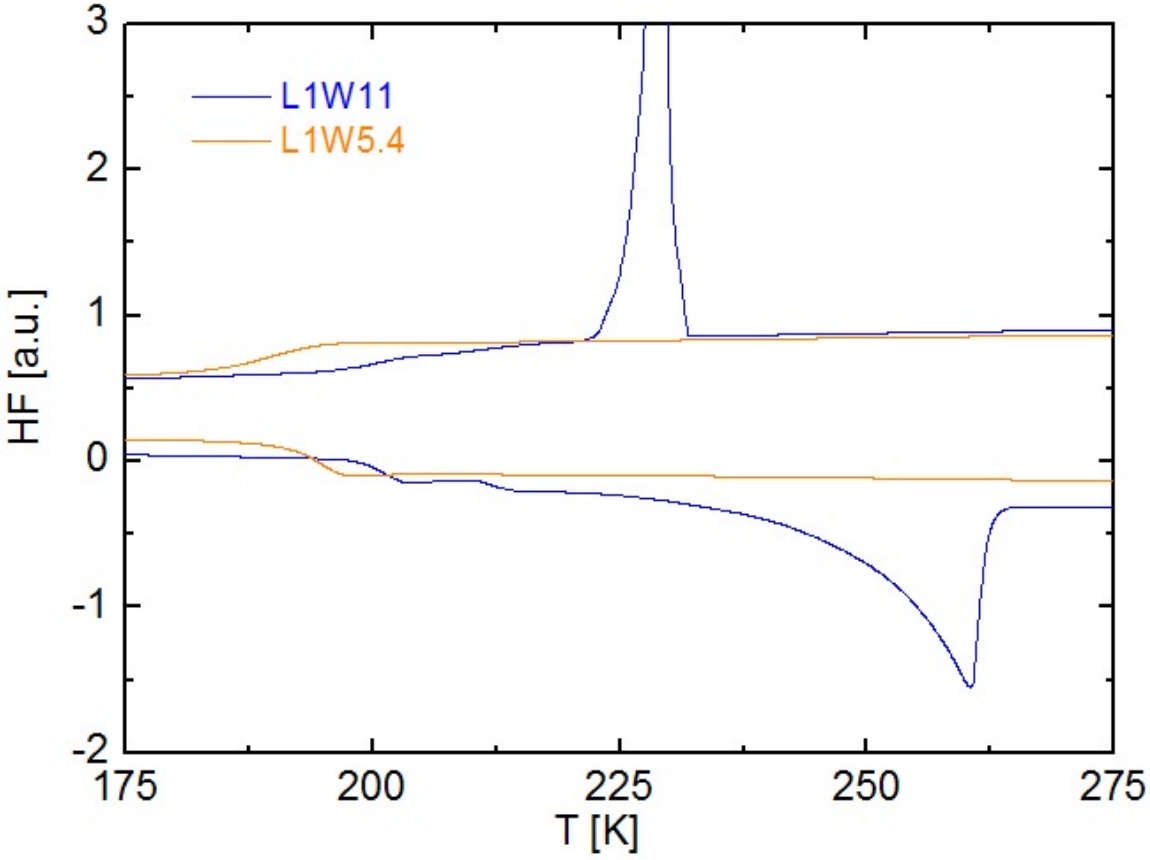
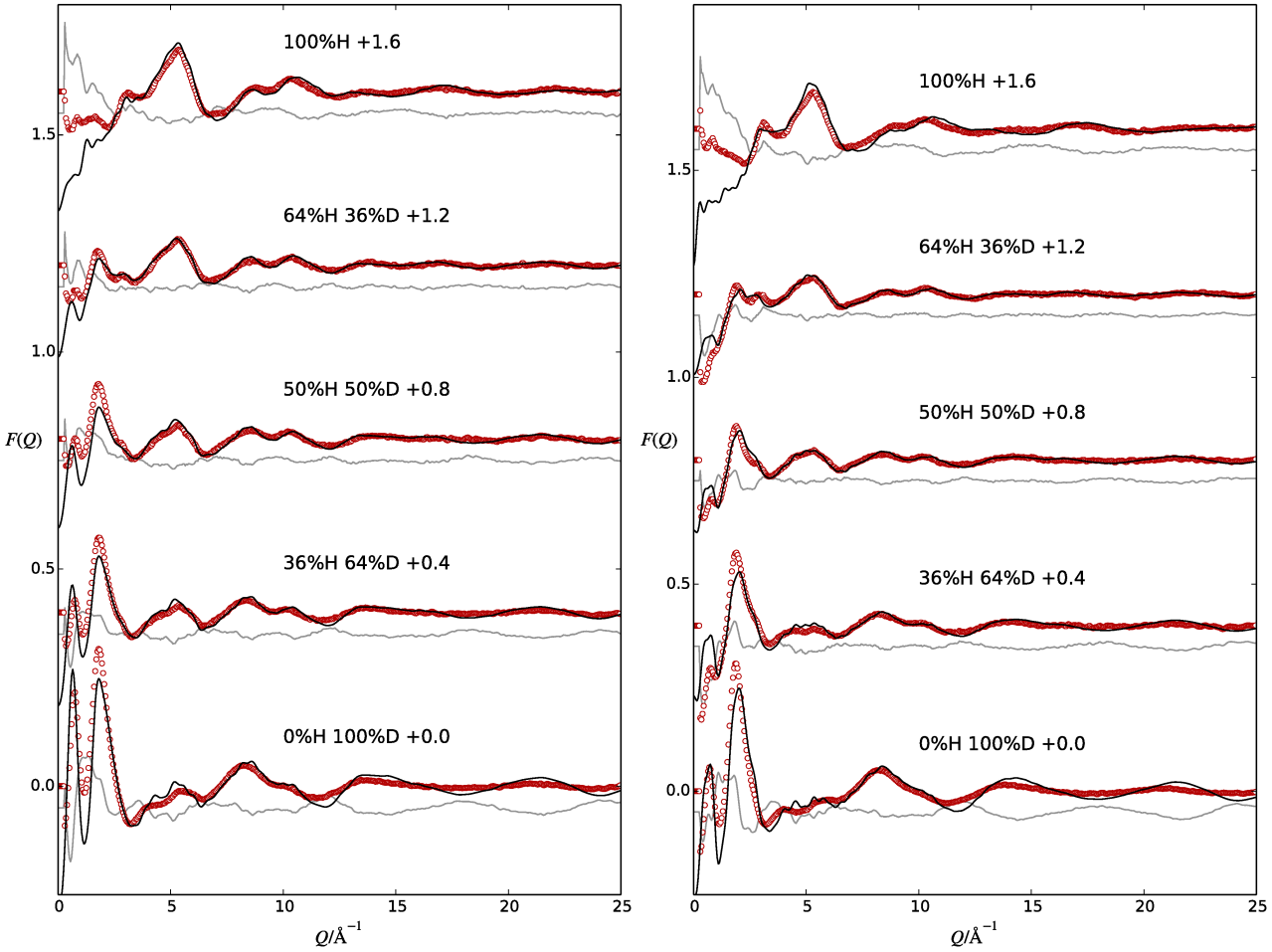


Fig. S1 (color online) Calorimetric response of lysine/water solutions at the two water concentrations analyzed in this work. L1W11 shows crystallization on cooling whereas L1W5.4 is amorphous in the whole temperature interval.



(a) Unsaturated mixture of 5.4 water molecules per lysine molecule (L1W11)

(b) Saturated mixture of 11 water molecules per lysine molecule (L1W5.4)

Fig. S2 (color online). Measured neutron diffraction data (dots), $F(Q)$ from molecular dynamics (black lines) and the difference (gray lines) with the deuterium/hydrogen proportions described in the methods section. The data have been translated vertically in increments of 0.4 for clarity

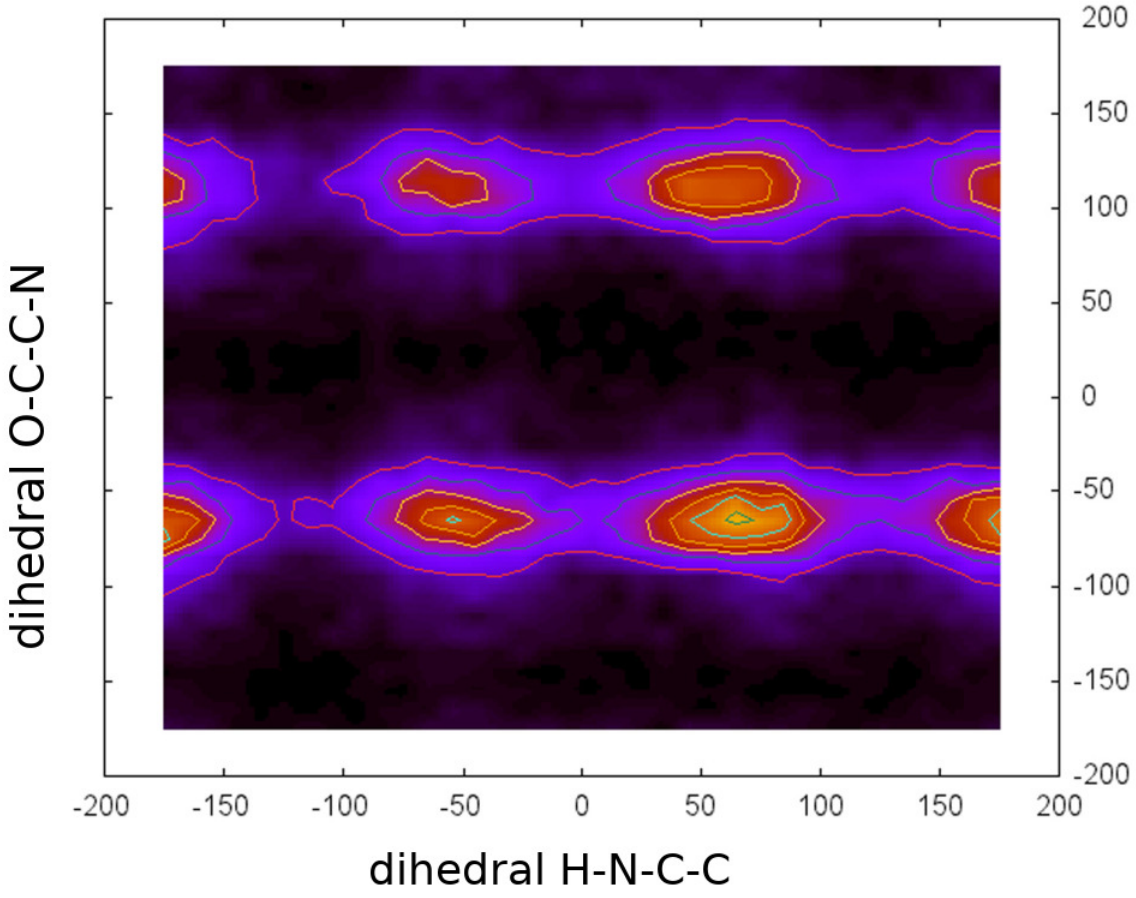


Fig. S3 (color online) Dihedral angles characterizing the orientation of the hydrogens pertaining to the amine group and the oxygens of the carboxyl group of lysine. Internal hydrogen bonds would be characterized by angles of 0 degrees.

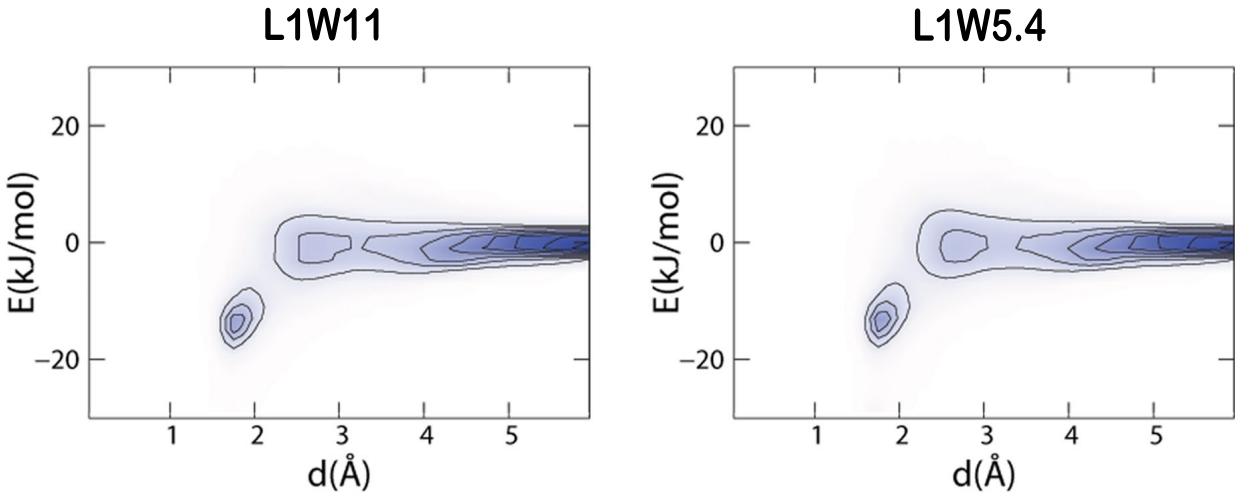


Fig. S4 (color online) Probability distribution functions of the distance between molecular surfaces of LYS0 and waters as a function of the contact energy $g^{SS}_{LYS0,water}(d,E)(d)$. The spot with negative energy corresponds to hydrogen bonded molecules (most probably through O-H_W contacts), while the spot between 2-3 Å with zero energy would correspond to water molecules close to the backbone of lysine without hydrogen bonds. These water molecules cause the H_b-H_W and H_b-O_W contacts in Fig. 6 of the main text, and they are free to form crystal clusters.

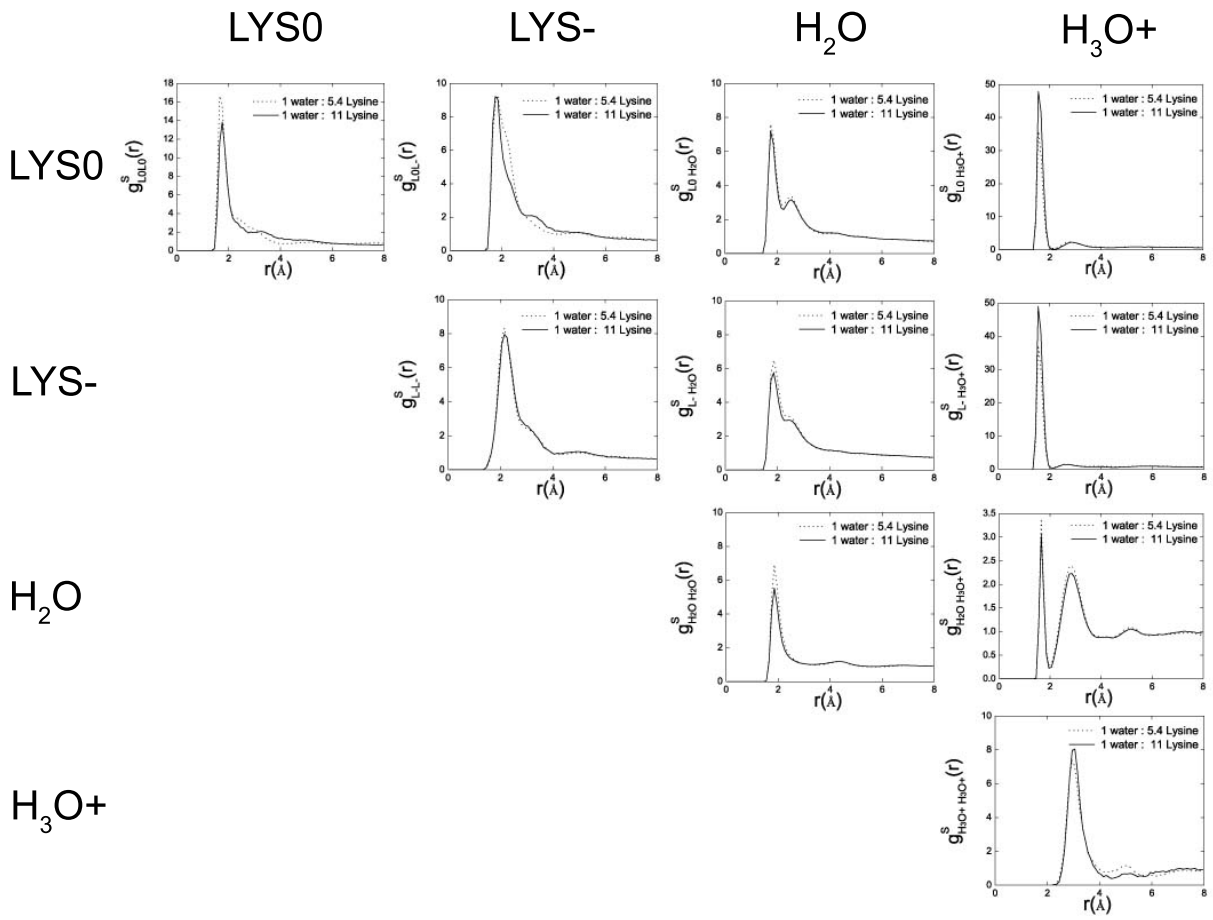
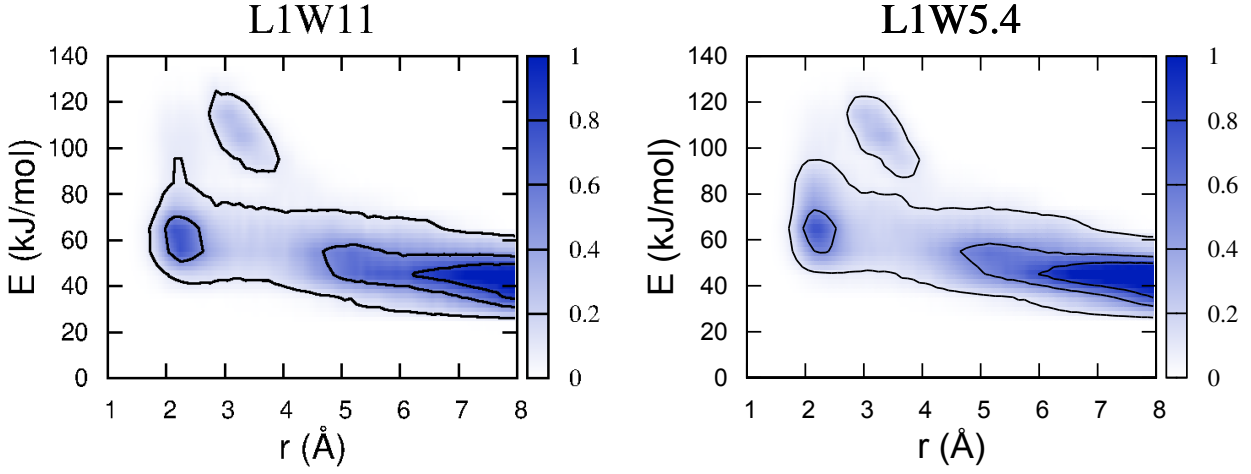


Fig. S5 Surface Surface Distance Distribution functions for all possible combinations between the molecular species of both mixtures L1W5.4 and L1W11 (dashed and solid respectively): $g^{SS}_{i,j}(d)$, being i,j=LYS0,LYS-, H_2O, and H_3O^+.



(a) Unsaturated mixture of 11 water molecules per lysine molecule (L1W11)

(b) Saturated mixture of 5.4 water molecules per lysine molecule (L1W5.4)

Fig. S6 (color online). Probability distribution functions of the distance between molecular surfaces of LYS- and LYS- as a function of the contact energy $g^{SS}_{LYS-,LYS-}(d,E)(r)$. The energy maps are identical for both solutions a) L1W11 and b) L1W5.4. This, along with the identical $g^{SS}_{LYS-,LYS-}(d)$ distributions for both concentrations in Fig. S3 prove that the differences between mixtures do not come from LYS-LYS- molecules.

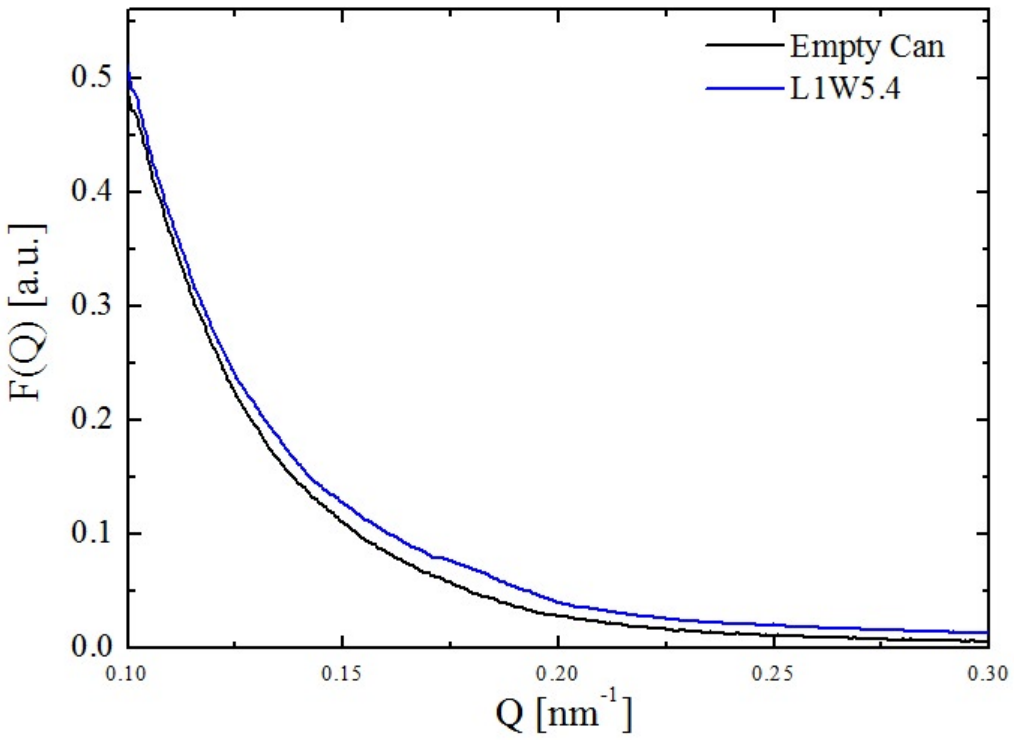


Fig. S7 (color online) Small-angle scattering data of 1-Lysine (L1W5.4). The empty can is also included. The small-angle scattering observed is coming from the sample container as evidenced by the fact that the empty capillary shows similar intensity increase towards low Q