Supporting Information: Atomistic Understanding of Zeolite Nanosheets for Water Desalination

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Introduction

In this document, we provide the results of the simulations, i.e., the water permeability and salt rejection of the studied zeolites, and the force field parameters, as well as the free energy profiles of water in all investigated zeolites.

Water permeability and salt rejection

The postprocessed results of MD simulations are summarized in Table S1. In this table, the type of channels for each zeolite (1-dimensional, multi-dimensional, or cage-like) and the direction in which water permeates are provided in the first column. The name of the zeolites is in the second column. The third column shows the density of silanol groups on the surface of the membranes, and the fourth one provides the density of channels per area of zeolite. The maximum included sphere diameter (D_i) in column 5, the pore-limited diameter (PLD or d_f) in column 6, the minimum opening width of the channel (d_min) in column 7 and the maximum opening width of the channel (d_max) in column 8 are listed. The maximum included sphere diameter is the diameter of the largest sphere which can be included inside a structure.[1] The PLD is the diameter of the largest sphere diffusing through a channel.[1] These diameters are obtained from the IZA database.[2] The 9^th column in Table S1 is the cross-sectional area of the channel, calculated from the area of an ellipse with the major and minor diameters equal to the maximum and minimum opening widths of the main channel. The thickness of the slab of the bulk zeolite without any hydroxyl group is reported in the 10th column. For a better comparison of the water permeabilities, the thickness of the zeolites have been chosen to be approximately 25 Å (small variation exists, between 20 Å and 30Å). The outcome of the simulations are the water permeability as well as the salt rejection, which are provided in the last three columns. The water permeability (K/L) is

defined as follows:

$$J = \frac{K \cdot A \cdot \Delta P}{L} \rightarrow \frac{K}{L} = \frac{J}{A \cdot \Delta P} = \frac{J}{A \cdot (P - \Pi_{\text{osmotic}})} \tag{S1}$$

J is the water flow rate through a membrane. A is the area of the membrane. P and Π_{osmotic} are the applied transmembrane pressure and the osmotic pressure of the solution, respectively. The salt rejection is defined as the ratio of the number of passed ion pairs to the initial number on the feed side when half of the water molecules have permeated.

Force field parameters

The force field parameters for bonded and non-bonded potentials are available in Tables S2 to S4. A quadratic potential is used to describe both bond stretching and bond angle bending:

$$U_{\text{bond}} = K_r(r - r_0)^2 \tag{S2}$$

$$U_{\text{bend}} = K_\theta(\theta - \theta_0)^2 \tag{S3}$$

where K_r and K_θ are the force constants. r_0 and θ_0 are the equilibrium bond length and bond angle.

The non-bonded potential is the sum over all Lennard-Jones and Coulombic interactions of atoms between molecules or those separated by at least three bonds:

$$U_{\text{non-bonded}} = U_{\text{LJ}} + U_{\text{coul}} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}} \tag{S4}$$

where r_{ij} is the distance between two non-bonded atoms or sites. ϵ_{ij} and σ_{ij} are the Lennard-Jones parameters. q_i is the partial atomic charge. ϵ_0 is the permittivity of vacuum.

Free Energy Landscape in Non-Equilibrium MD Simulations

The free energy landscape of water molecules in a zeolite can be a determinate factor in controlling how easy water molecules can permeate. This free energy landscape is one of the outcomes of the non-equilibrium MD simulations. The relative probability/frequency of sampling oxygen atoms of water at a cross section perpendicular to the flow provides the information required for obtaining the free energy landscape:

$$A = \ln\left(\frac{P(q)}{P_{\text{ref}}}\right) \cdot k_B T \tag{S5}$$

where A is the free energy, k_B and T are the Boltzmann constant and temperature, respectively. $P(q)$ is the probability of observing an oxygen atom of water at a specific cross section (q). The reference position is where the minimum energy occurs. The free energy landscapes for all zeolites are provided in Figures S1 to S31. The multi-dimensional channel zeolites show a more complex free energy landscape than 1-dimensional channel zeolites.

Table S1: The postprocessed results of MD simulations for all investigated zeolites.

Type	Name	OH density [# / nm^2]	pore density [# / nm^2]	D_i [Å]	d_f [Å]	d_min [Å]	d_max [Å]	channel area [Å^2]	Thickness [Å]	K/L per area [lit/day/MPa/cm^2]	K/L per pore [water/ns/MPa/pore]	Salt rej. [%]
1D (Y)	JRY	7.08	1.42	4.59	4.40	4.1	5.9	19.0	24.50	18.96	0.05	100
1D (X)	AEL	3.99	0.80	5.64	4.63	4	6.5	20.4	24.94	36.67	0.18	100
1D (X)	EUO	4.25	0.43	7.00	4.99	4.1	5.4	17.4	27.80	13.61	0.12	100
1D (X)	PSI	4.17	0.46	5.79	4.85	5	5.6	22.0	24.79	18.64	0.16	100
1D (Z)	TON	4.77	0.79	5.71	5.11	4.6	5.7	20.6	26.28	17.08	0.08	100
1D (X)	MTT	4.78	0.80	6.19	5.07	4.5	5.2	18.4	26.28	19.41	0.09	100
1D (X)	MFS	4.39	0.73	6.81	5.37	5.1	5.4	21.6	22.63	23.33	0.12	100
1D (Z)	GON	6.96	0.58	6.32	5.45	5.4	6.8	28.8	26.28	25.46	0.17	100
1D (X)	MRE	4.06	0.68	6.36	5.59	5.6	5.6	24.6	24.77	30.02	0.17	100
1D (Z)	SSY	4.44	0.63	7.10	5.75	5	7.6	29.8	26.29	31.49	0.19	97
1D (Z)	VET	4.70	0.59	6.39	5.98	5.9	5.9	27.3	24.74	31.99	0.21	100
1D (X)	EZT	4.40	0.73	6.57	6.13	6.5	7.4	37.8	20.47	29.56	0.16	100
1D (Z)	SAF	4.13	0.52	6.66	6.19	5.6	8.5	37.4	24.95	39.35	0.30	99
1D (Z)	OSI	4.67	0.58	6.66	6.28	5.2	6	24.5	26.34	30.48	0.20	99
1D (Z)	ATS	4.22	0.70	7.30	6.82	6.5	7.5	38.3	26.29	43.12	0.24	92
2D (Z)	FER	4.41	0.74	6.31	4.69	4.2	5.4	17.8	22.62	24.01	0.13	100
3D (X)	MFI	3.08	0.77	6.36	4.70	5.1	5.5	22.0	20.09	22.67	0.11	100
3D (Y)	MFI	6.19	0.76	6.36	4.46	5.3	5.6	23.3	19.74	17.10	0.09	100
2D (X)	NES	5.04	0.63	7.04	5.07	4.8	5.7	21.5	26.06	22.14	0.14	100
2D (X)	NES	4.03	0.67	7.04	5.07	4.8	5.7	21.5	27.77	21.71	0.13	100
3D (X)	MEL	2.93	0.73	7.72	5.19	5.3	5.4	22.5	20.27	30.95	0.16	100
2D (Z)	SFG	6.23	0.62	6.96	5.38	5.2	5.7	23.3	26.13	22.02	0.14	100
3D (Z)	IWR	5.66	0.71	7.48	5.91	5.8	6.8	31.0	25.35	23.37	0.13	99
3D (Z)	BEC	3.68	0.61	6.95	6.09	6.3	7.5	37.1	25.95	31.51	0.20	95
3D (X)	BEC	6.03	0.60	6.95	6.09	6	6.9	32.5	25.54	18.46	0.12	100
3D (Z)	SAO	4.43	0.55	8.64	6.79	7	7	38.5	21.86	37.78	0.26	88
cage (Z)	KFI	2.32	1.16	10.67	4.04	3.9	3.9	11.9	18.58	15.29	0.05	100
cage (Z)	LTA	5.63	0.70	11.05	4.21	4.1	4.1	13.2	23.84	13.46	0.07	100
cage (Z)	OBW	3.26	0.47	9.26	5.18	5	5	19.6	27.83	14.49	0.12	100
cage (Z)	FAU	4.05	0.34	11.24	7.35	7.35	7.35	43.0	24.35	43.88	0.50	90

Table S2: Bond stretching potential parameters (Equation (S2)) for the water molecule and the zeolite surface.

Material	Bond	K_r (kcal/mol/Å^2)	r_0 (Å)
Water (TIP3P)[3]	H - O	rigid	0.9572
Zeolite membrane[4]	Si - O	495.0	0.945
	O - H	285.0	1.65

Table S3: Bond angle bending potential parameters (Equation (S3)) for the water molecule and the zeolite surface.

Material	Bond angle	K_θ (kcal/mol/rad^2)	θ_0 (deg)
Water (TIP3P)[3]	H - O - H	rigid	104.52
Zeolite membrane[4]	O - Si - O	100.0	109.5
	Si - O - Si	100.0	149.0
	Si - O - H	50.0	115.0

Table S4: Non-bonded potential parameters (Equation (S4)) for the water molecule, ions, and zeolite atoms.

Material	Name	(pseudo)atom	ϵ (kcal/mol)	σ (Å)	q
Water (TIP3P)[3]	Hydrogen	H	0.0	0.0	+0.417
	Oxygen	O	0.1521	3.1507	-0.834
Salt[5]	Sodium	Na	0.0874393	2.43928	+1.0
	Chloride	Cl	0.0355910	4.47766	-1.0
Zeolite membrane[4]	Silicon (bulk)	Si	0.093	3.697	+1.1
	Oxygen (bulk)	O	0.054	3.091	-0.55
	Oxygen (silanol)	O	0.122	3.091	-0.675
	Hydrogen (silanol)	H	0.015	0.967	+0.4

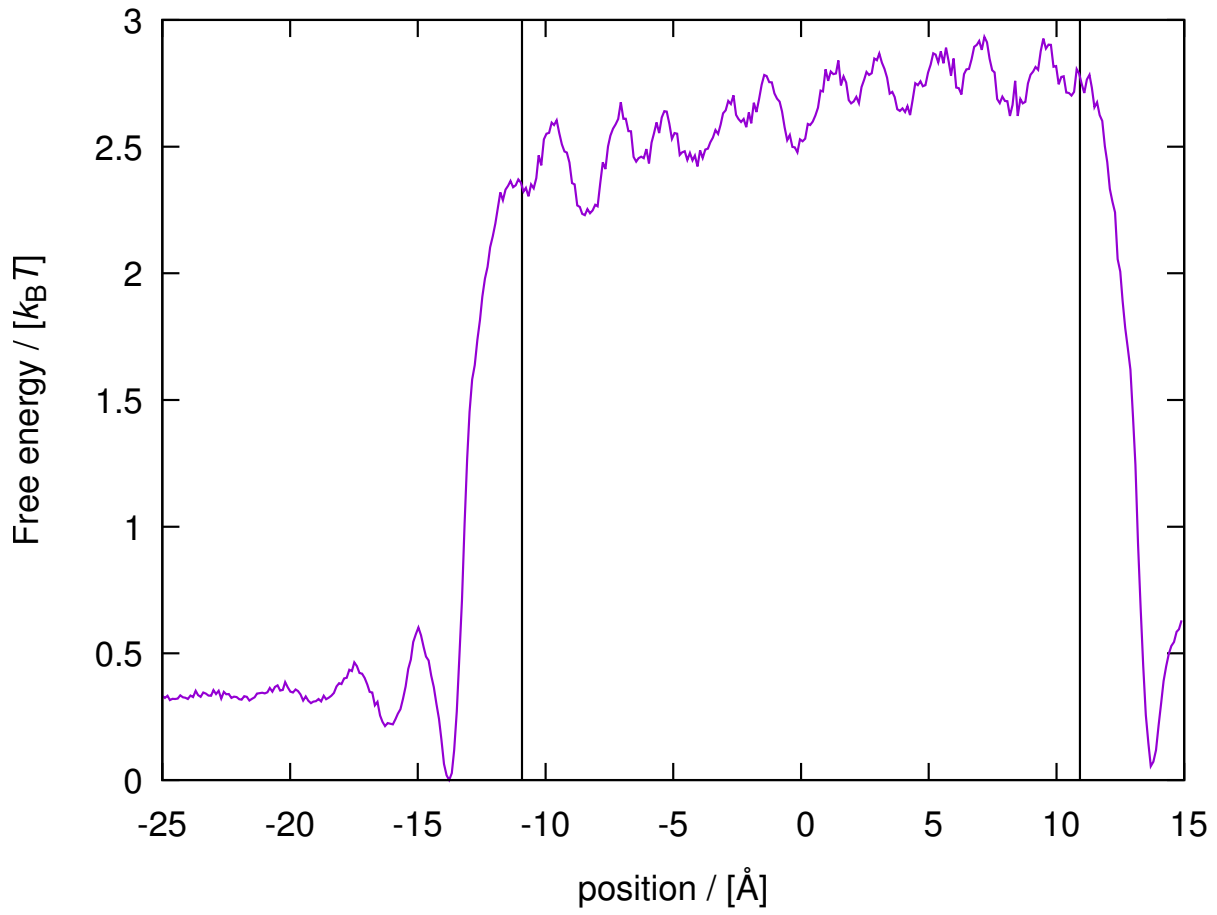

Figure S1: Free energy landscape of water molecules in AEL in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

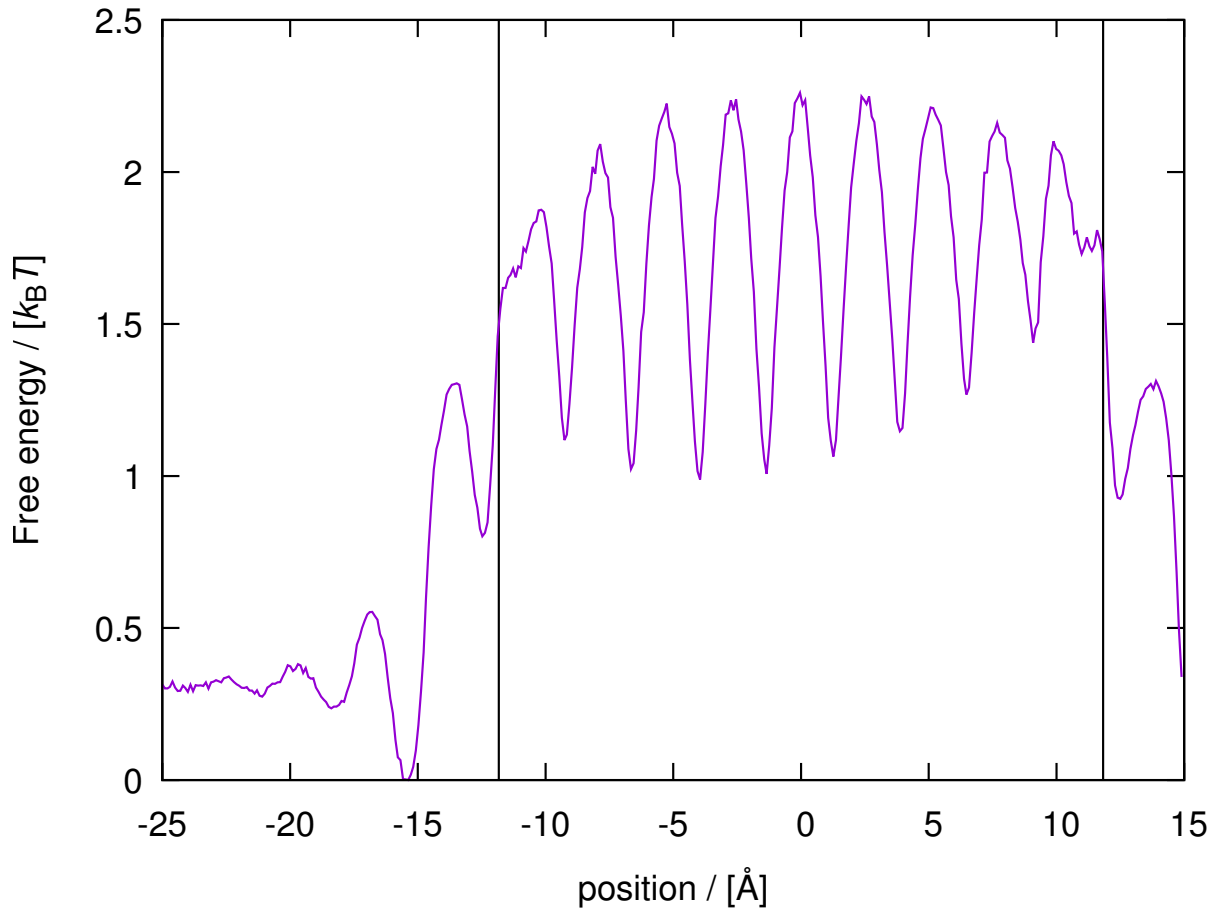

Figure S2: Free energy landscape of water molecules in ATS in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

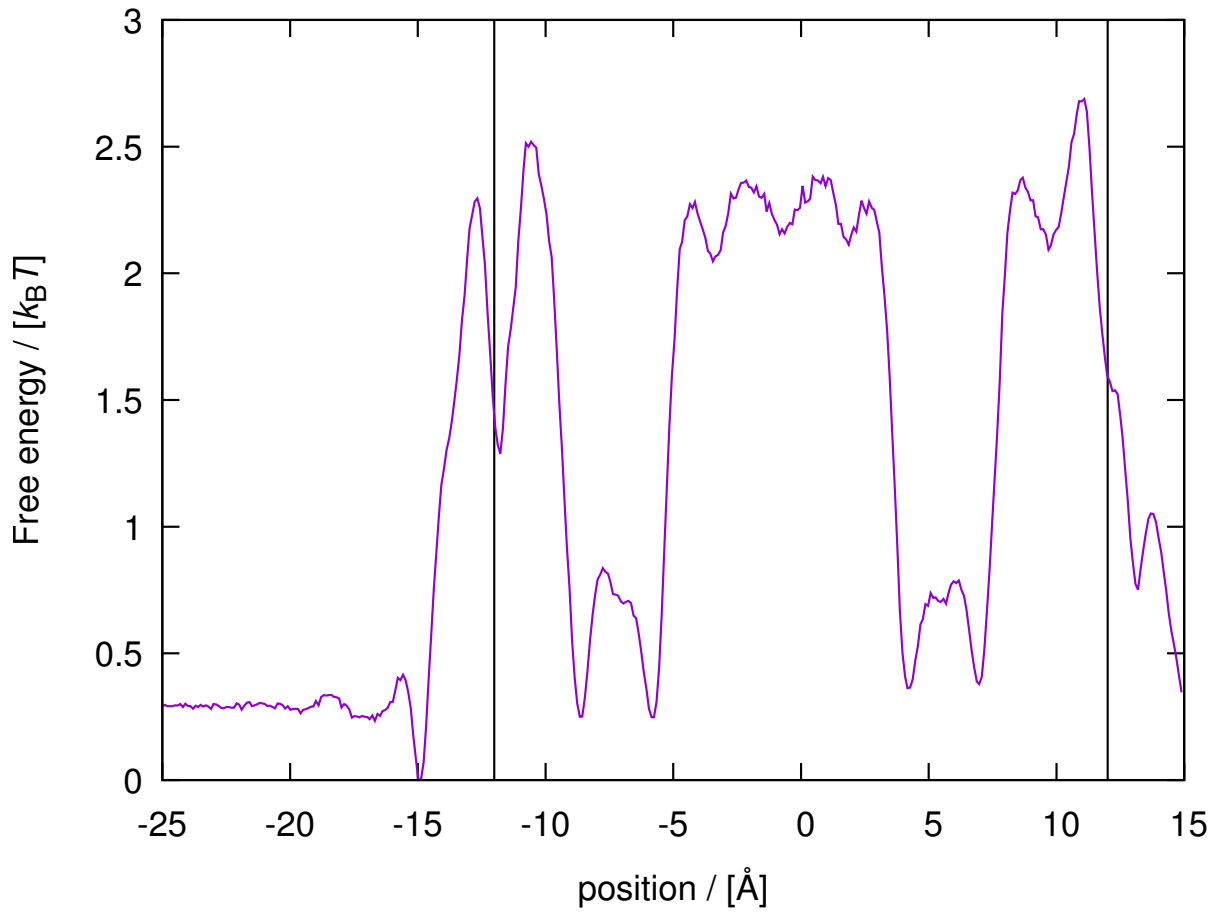

Figure S3: Free energy landscape of water molecules in BEC in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

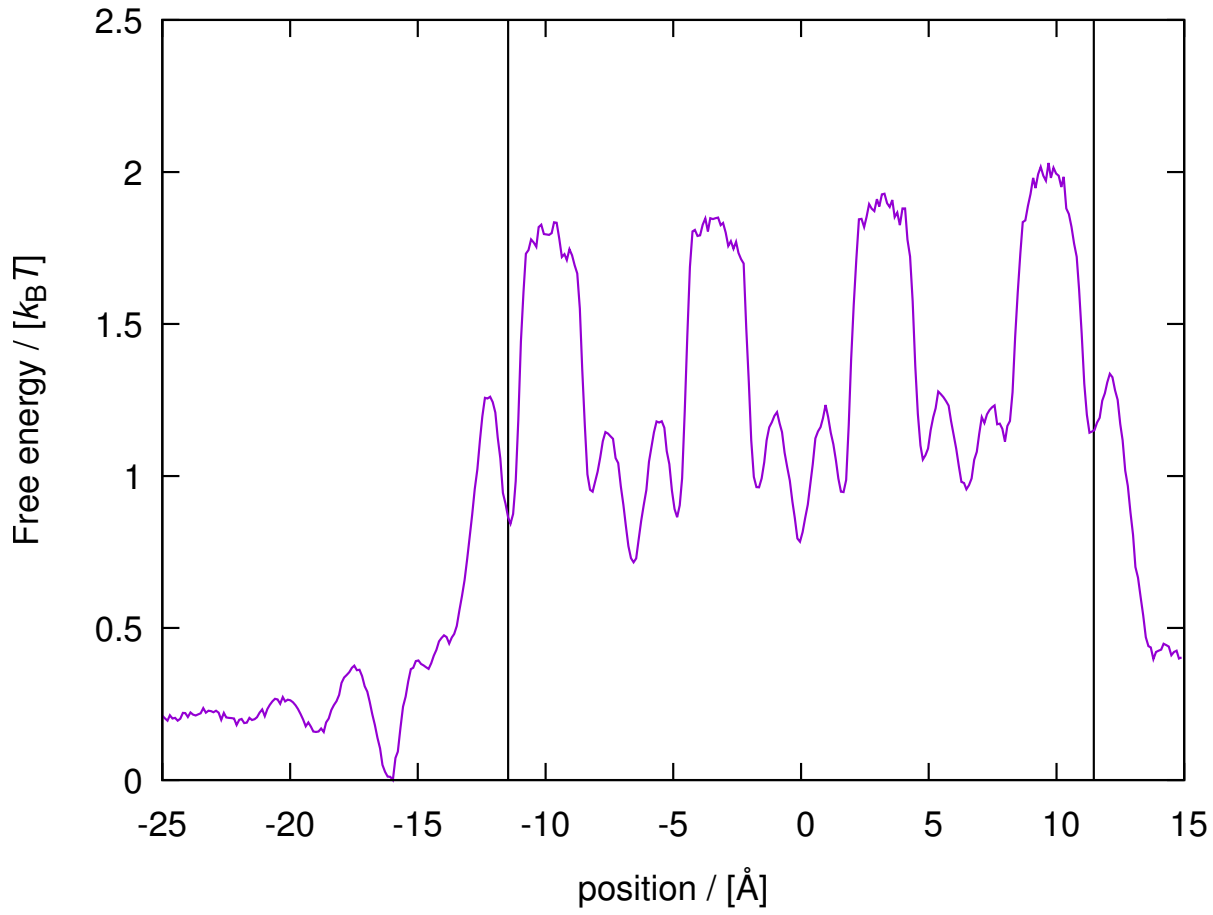

Figure S4: Free energy landscape of water molecules in BEC in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

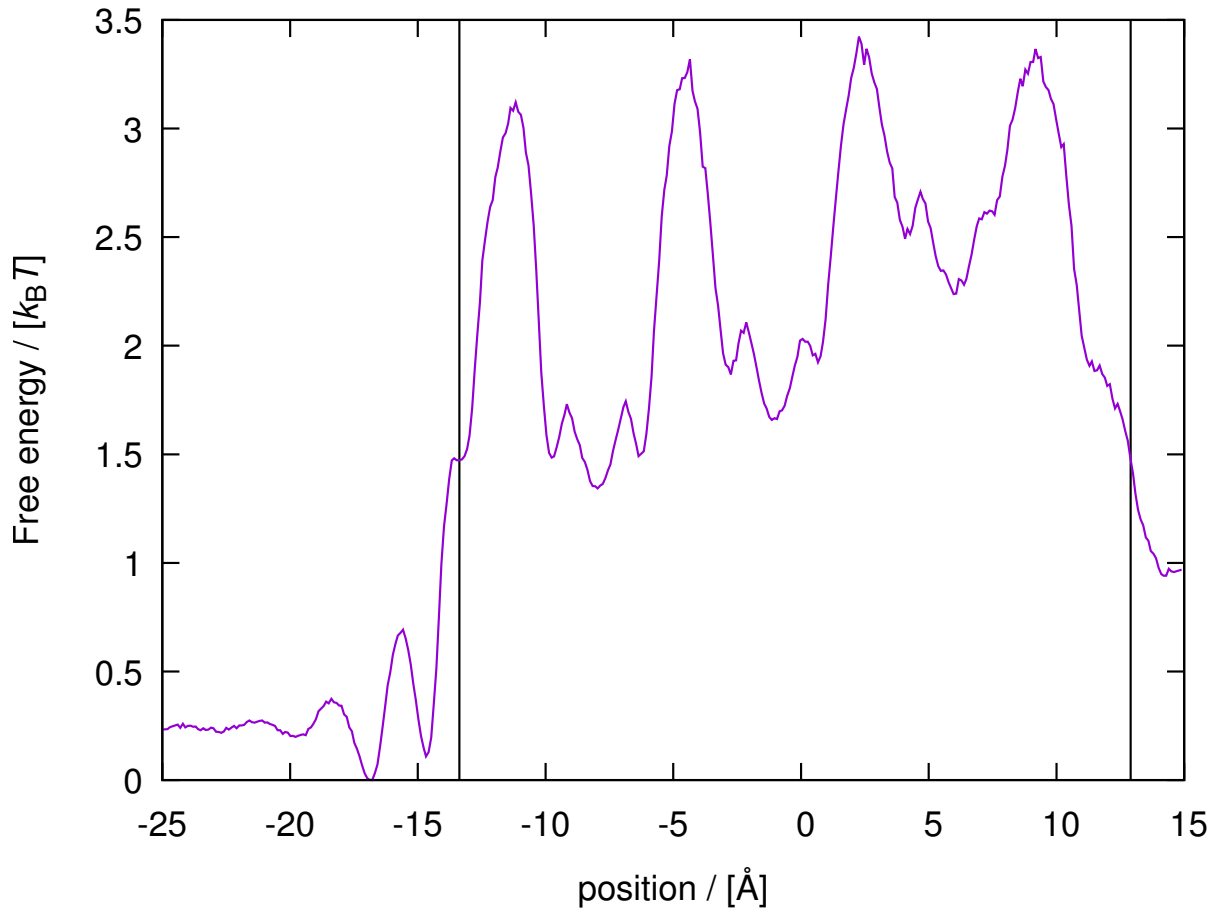

Figure S5: Free energy landscape of water molecules in EUO in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

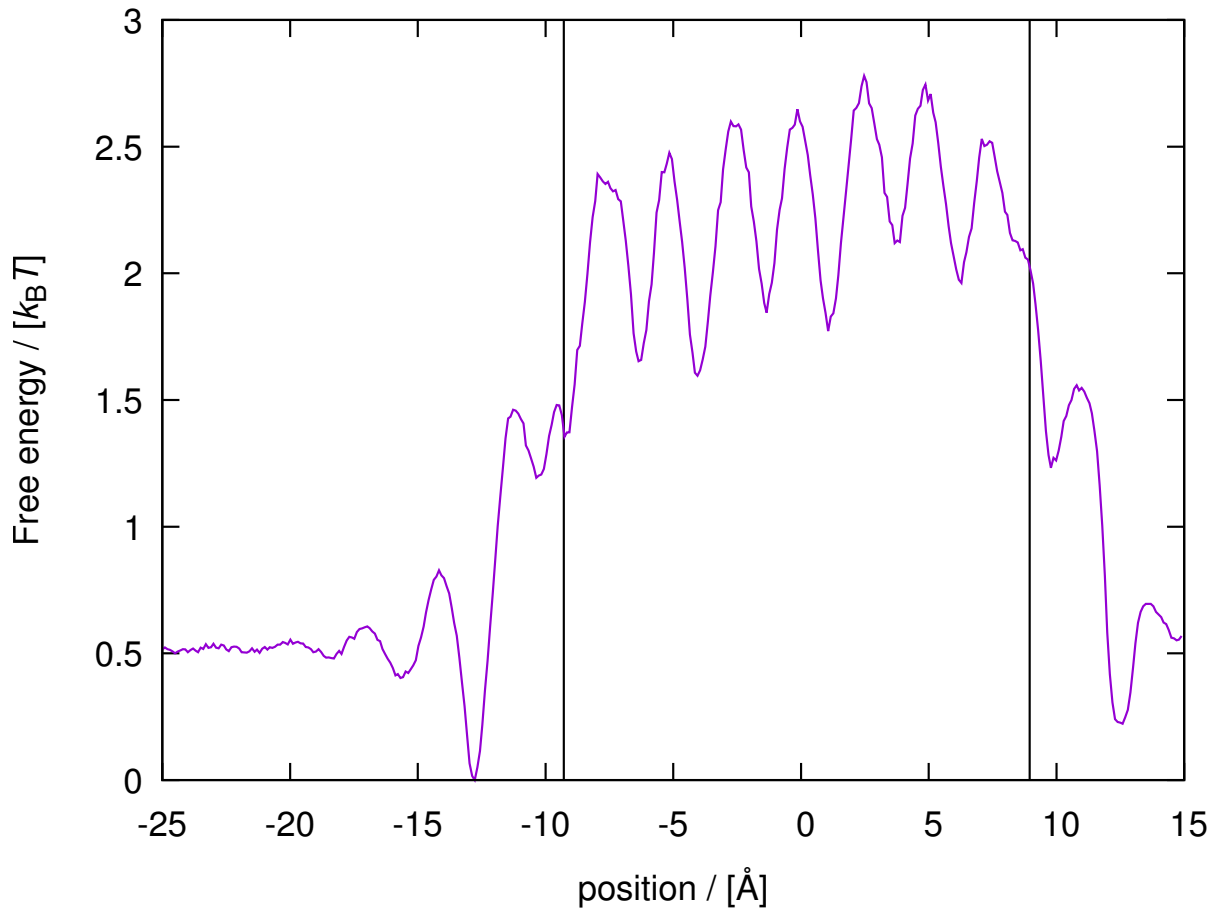

Figure S6: Free energy landscape of water molecules in EZT in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

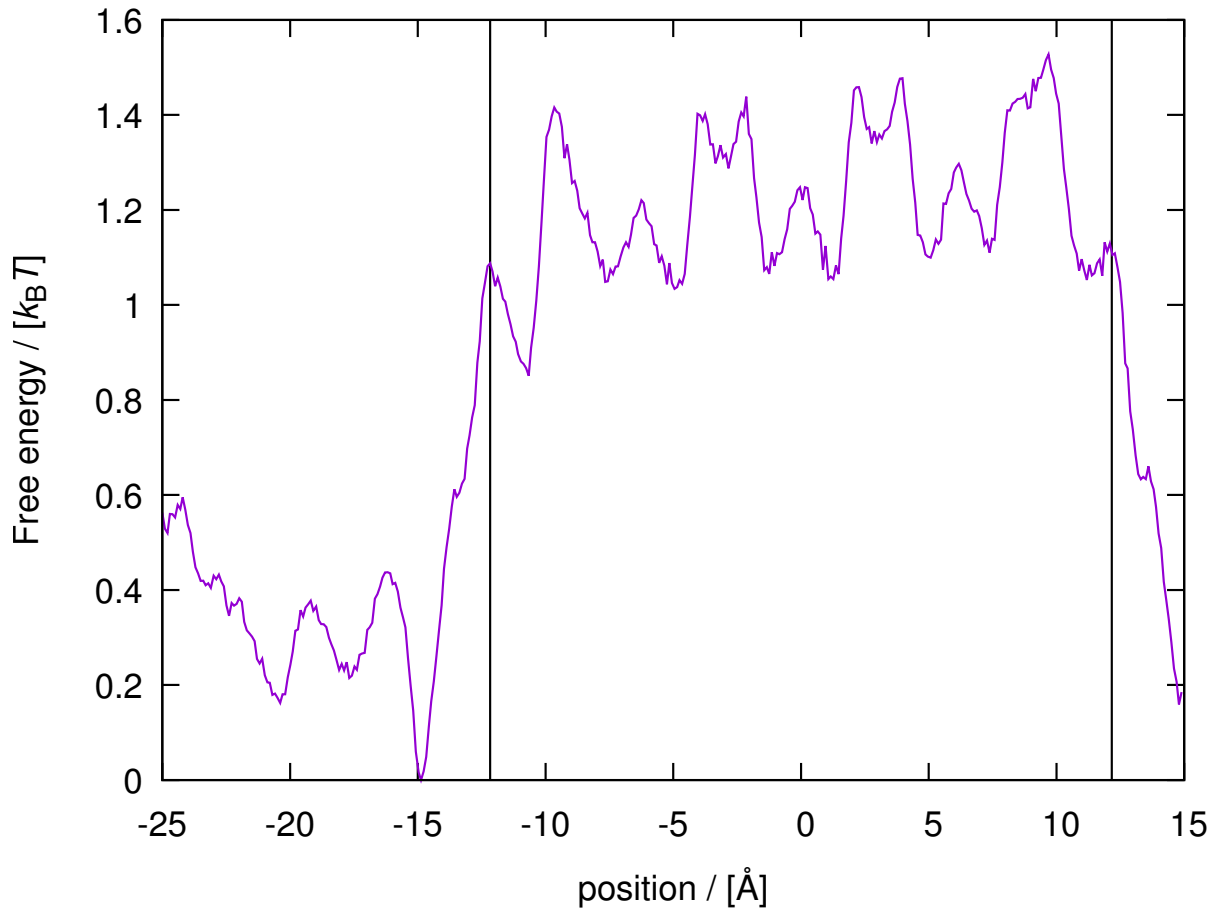

Figure S7: Free energy landscape of water molecules in FAU in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

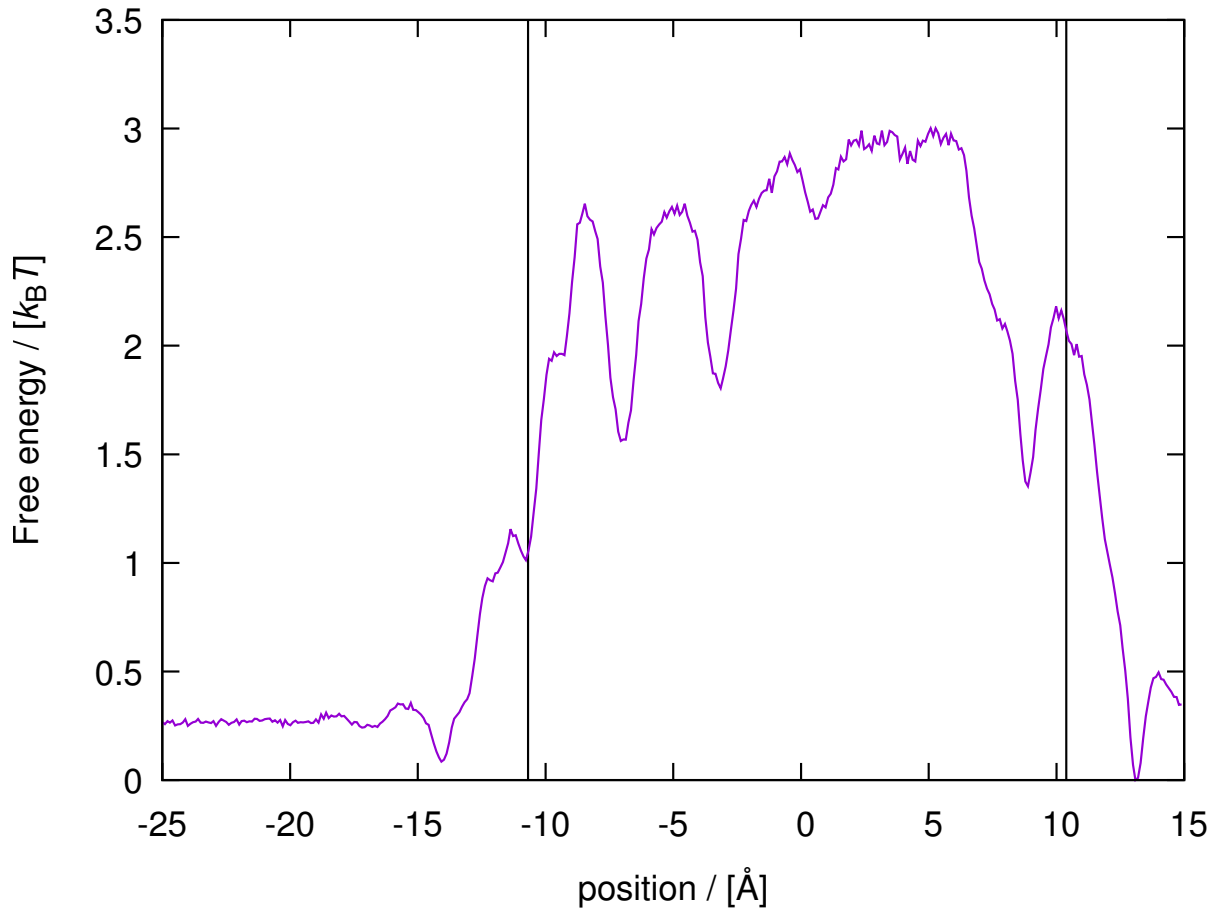

Figure S8: Free energy landscape of water molecules in FER in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

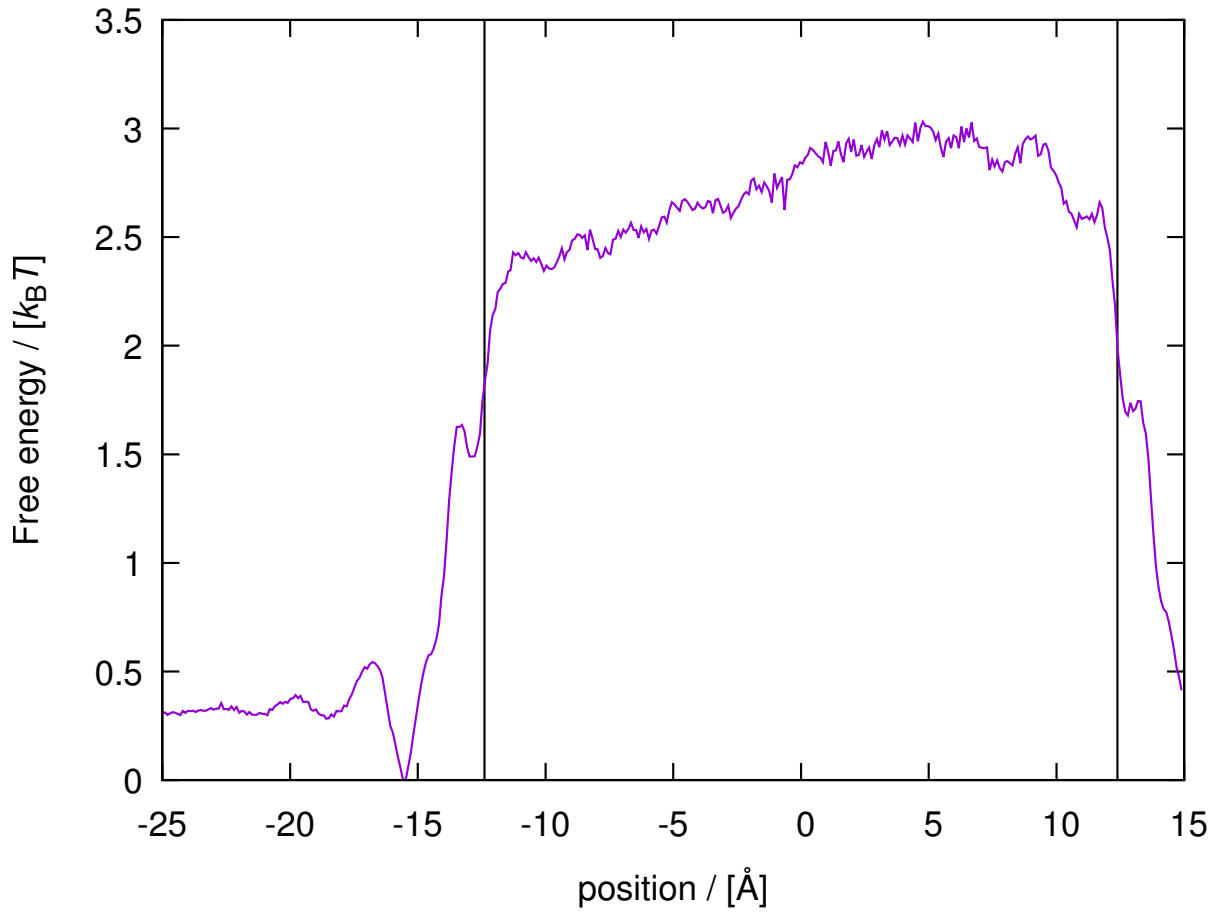

Figure S9: Free energy landscape of water molecules in GON in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

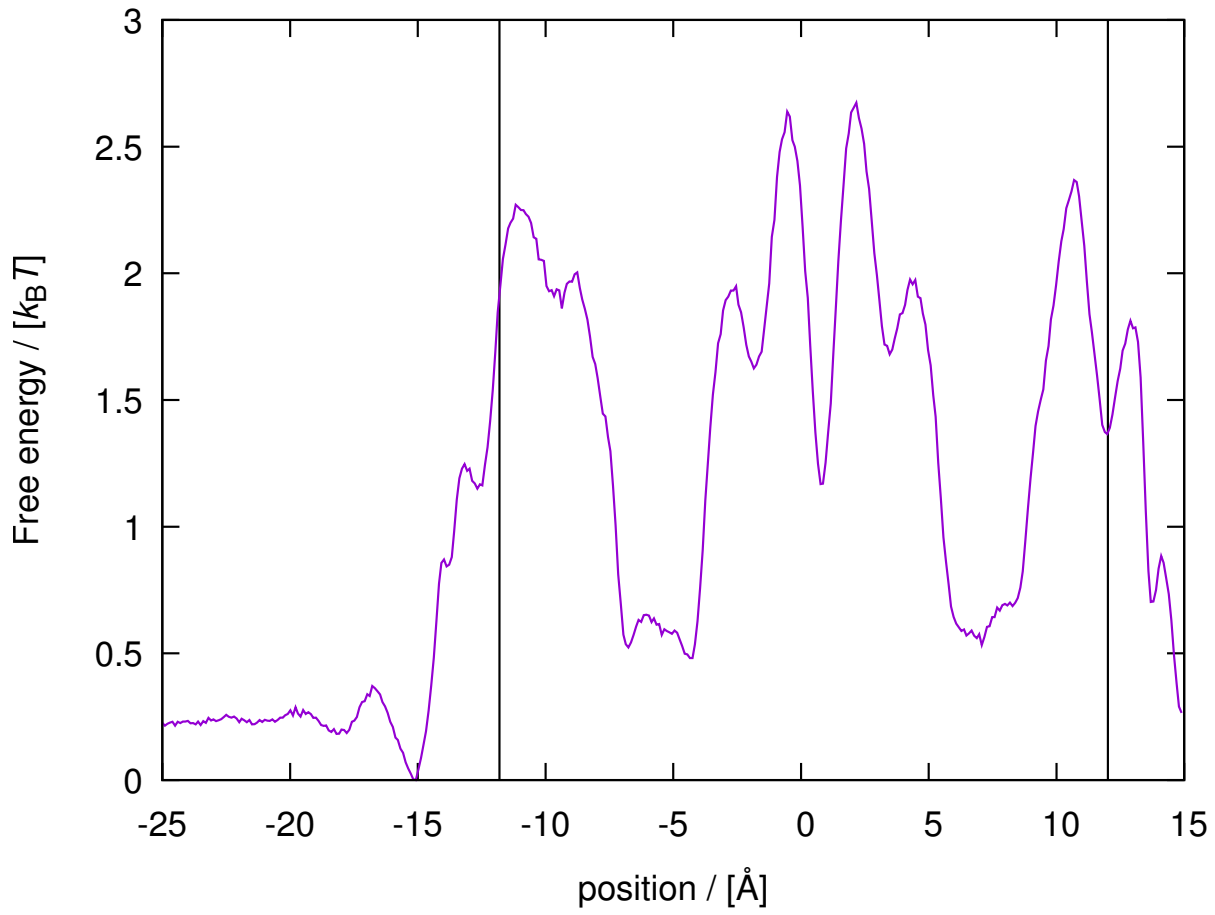

Figure S10: Free energy landscape of water molecules in IWR in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

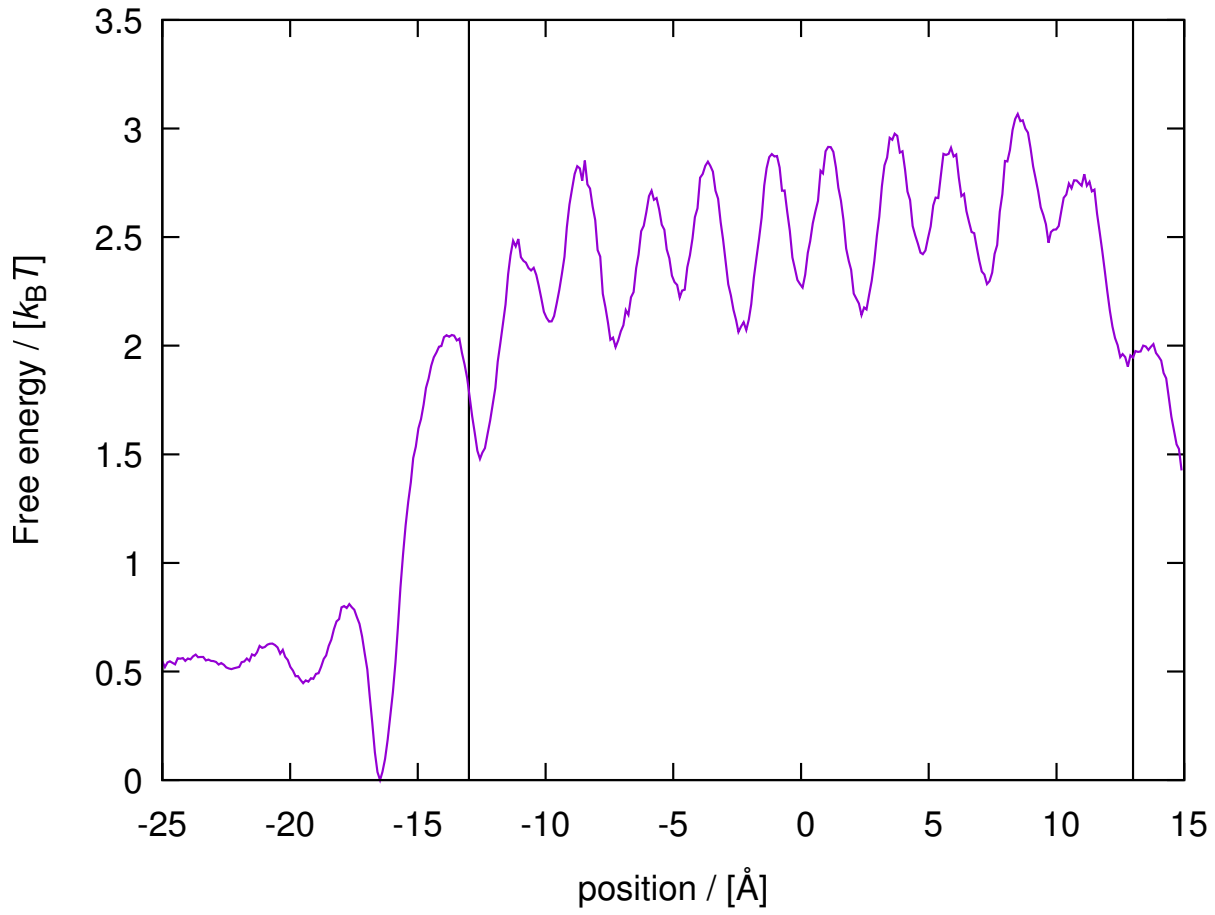

Figure S11: Free energy landscape of water molecules in JRY in the y direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

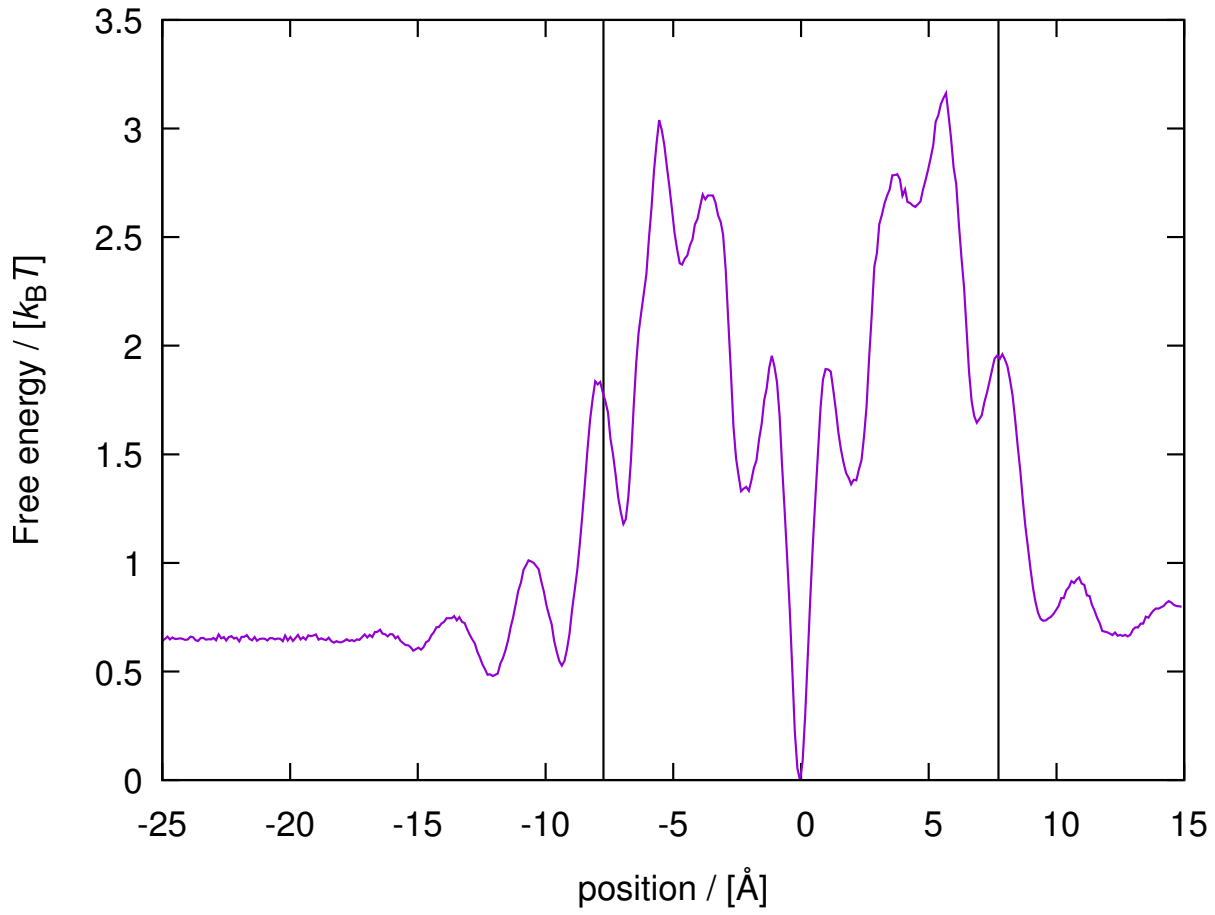

Figure S12: Free energy landscape of water molecules in KFI in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

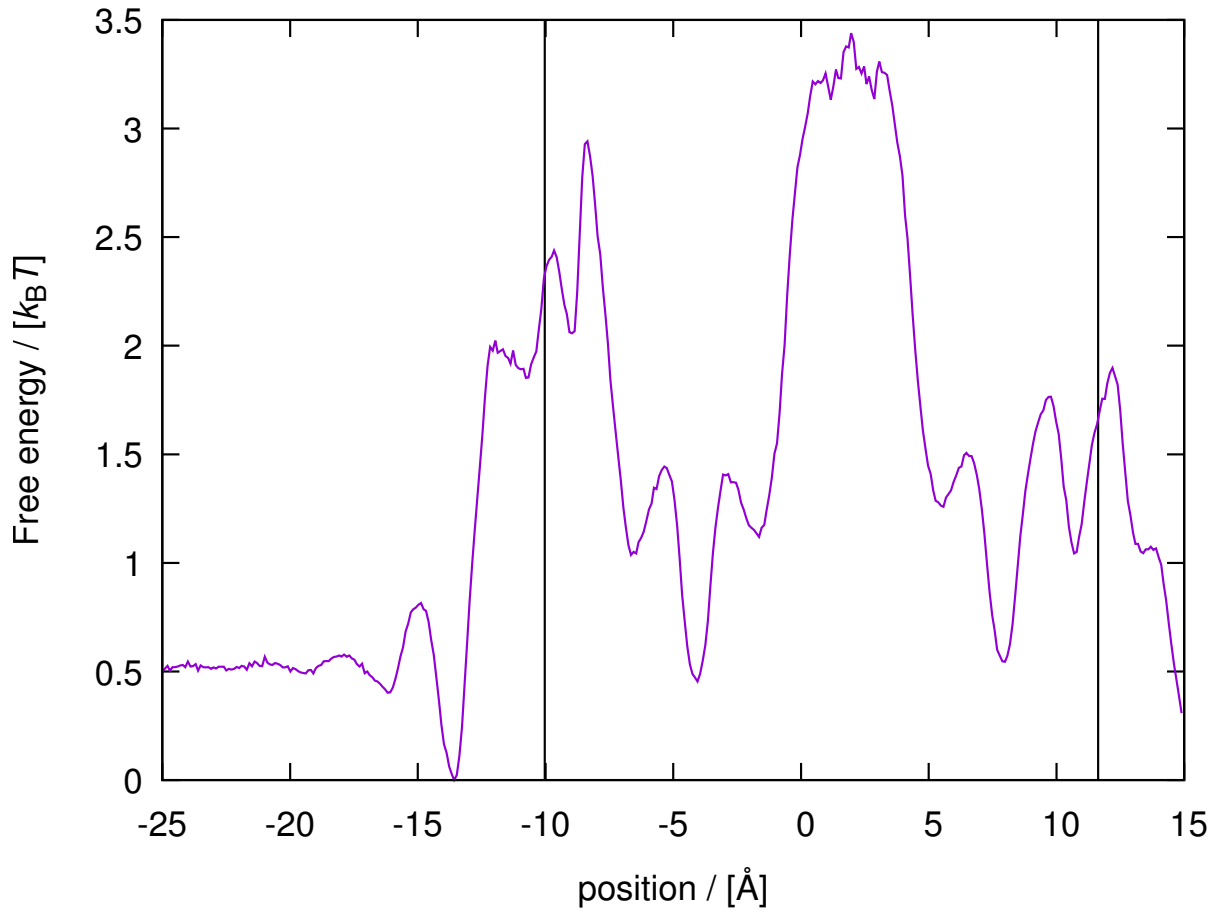

Figure S13: Free energy landscape of water molecules in LTA in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

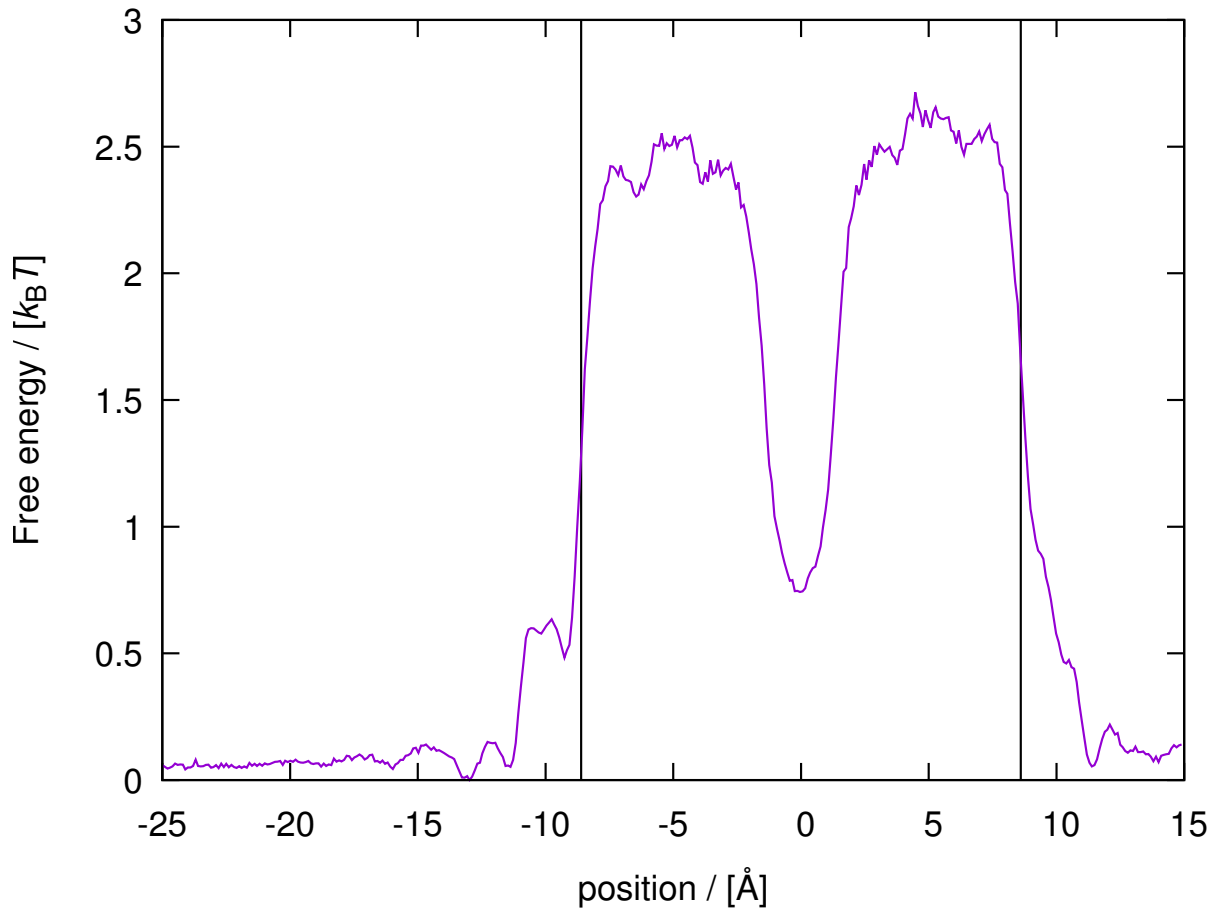

Figure S14: Free energy landscape of water molecules in ATS in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

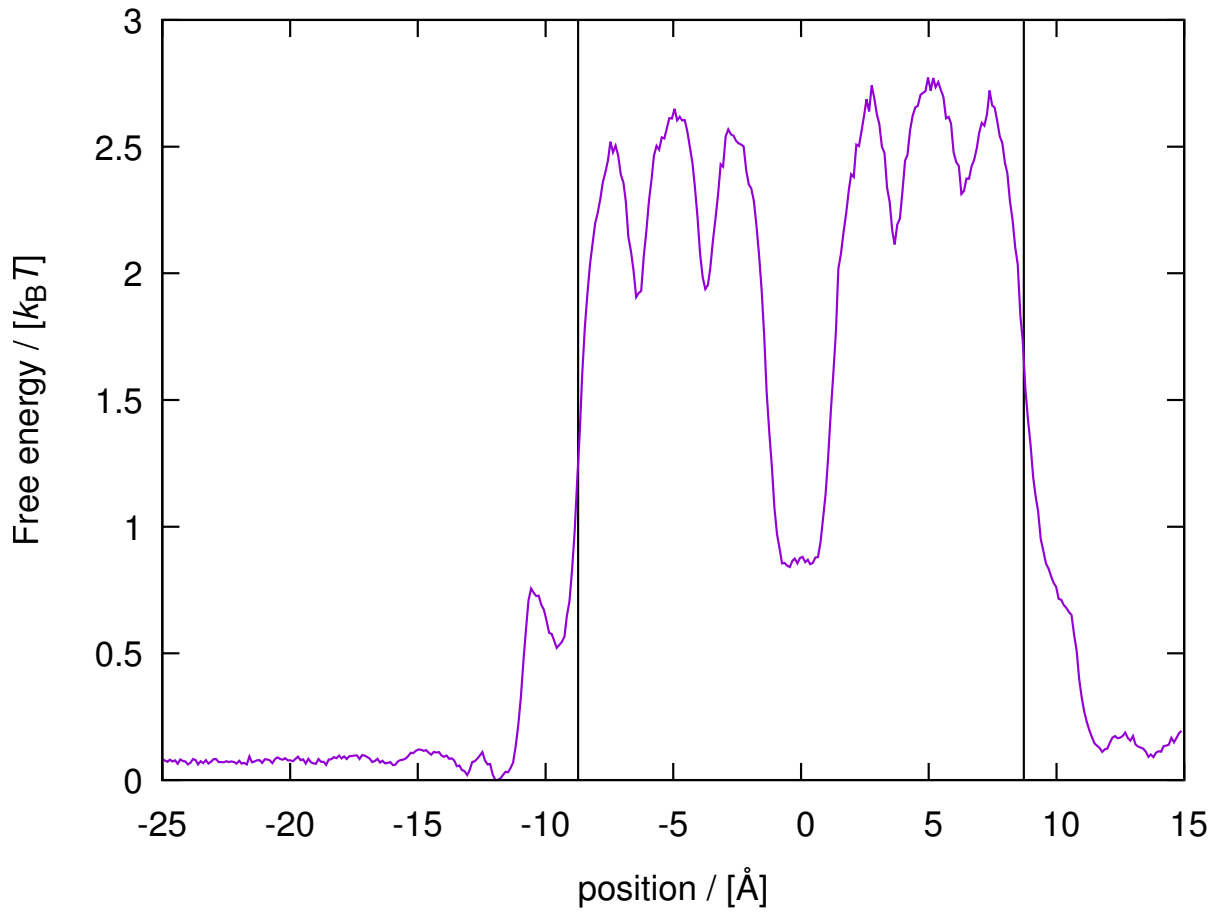

Figure S15: Free energy landscape of water molecules in MFI in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

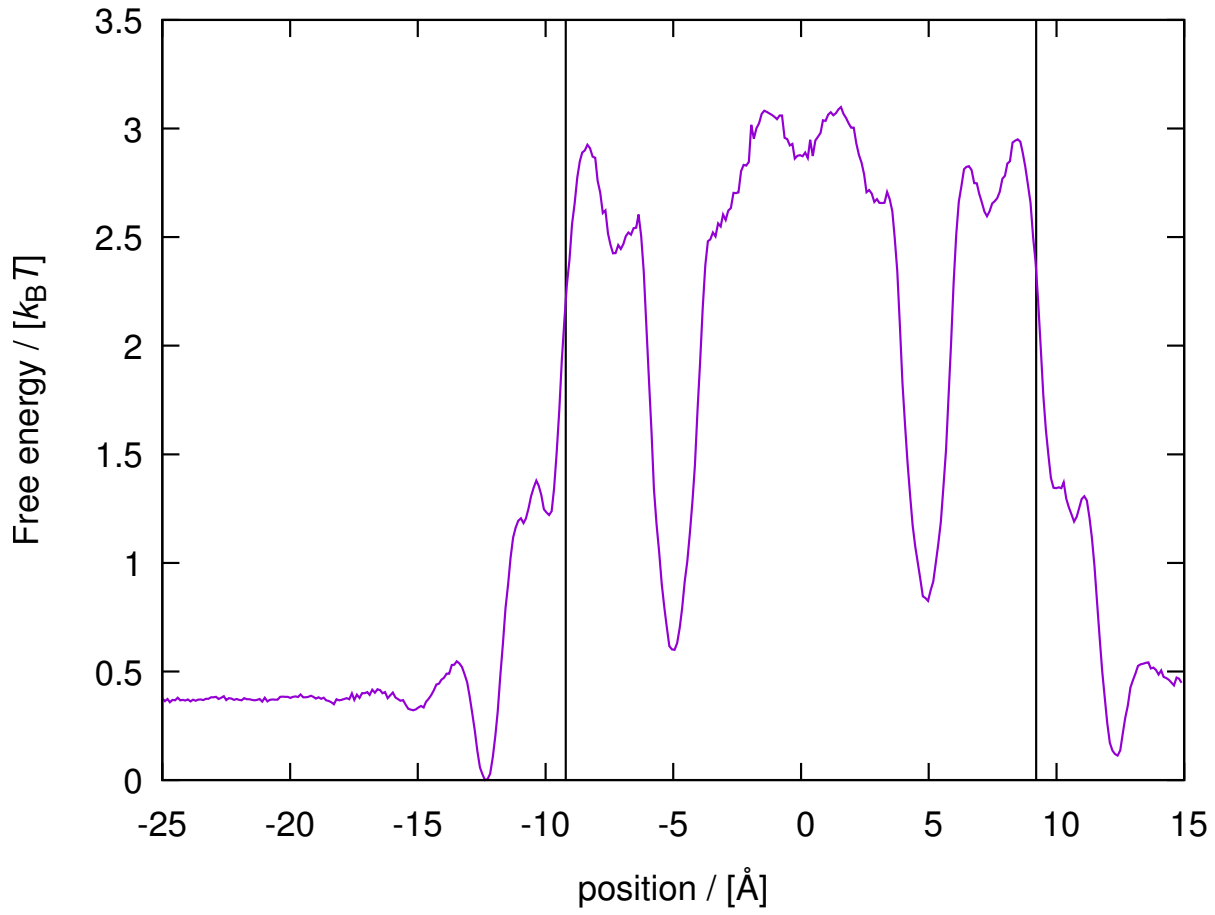

Figure S16: Free energy landscape of water molecules in ATS in the y direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

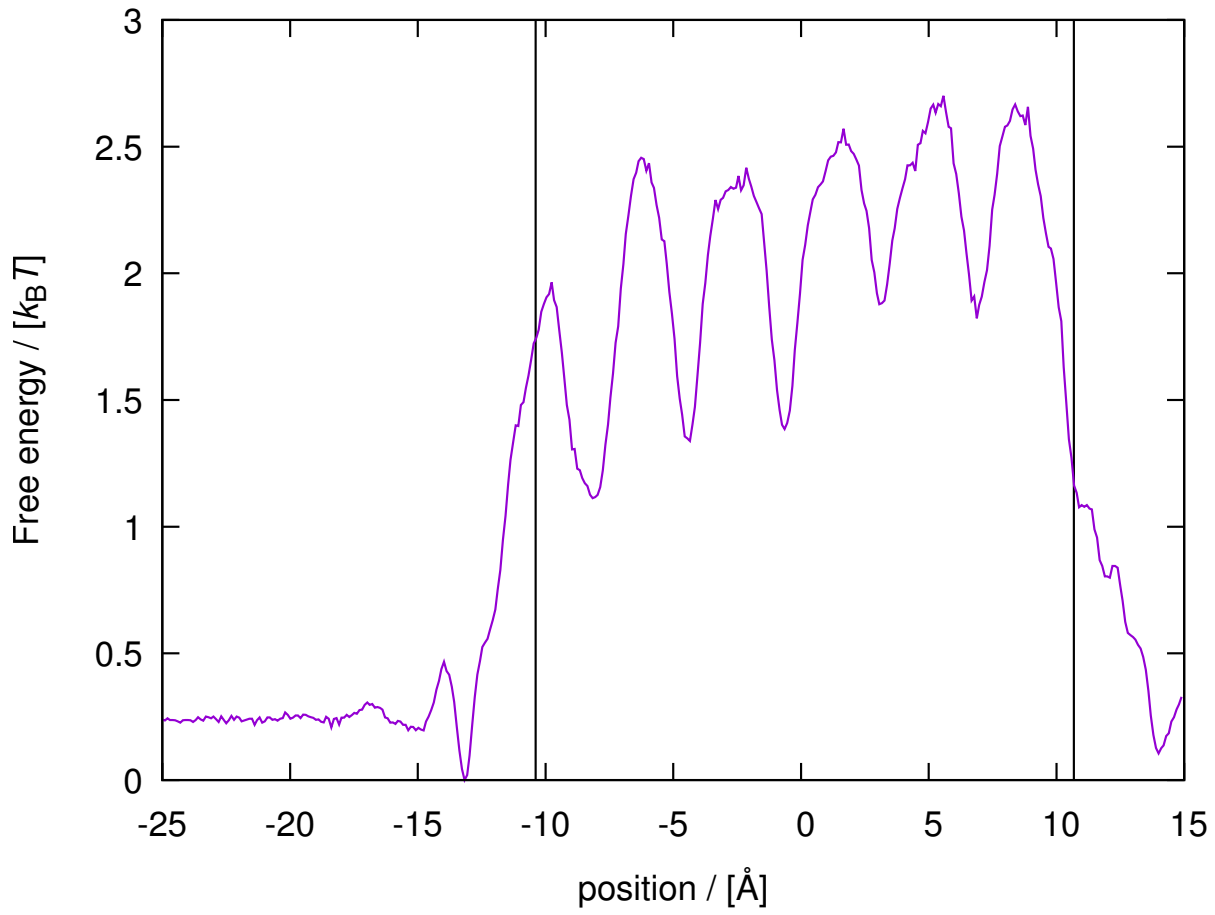

Figure S17: Free energy landscape of water molecules in MFS in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

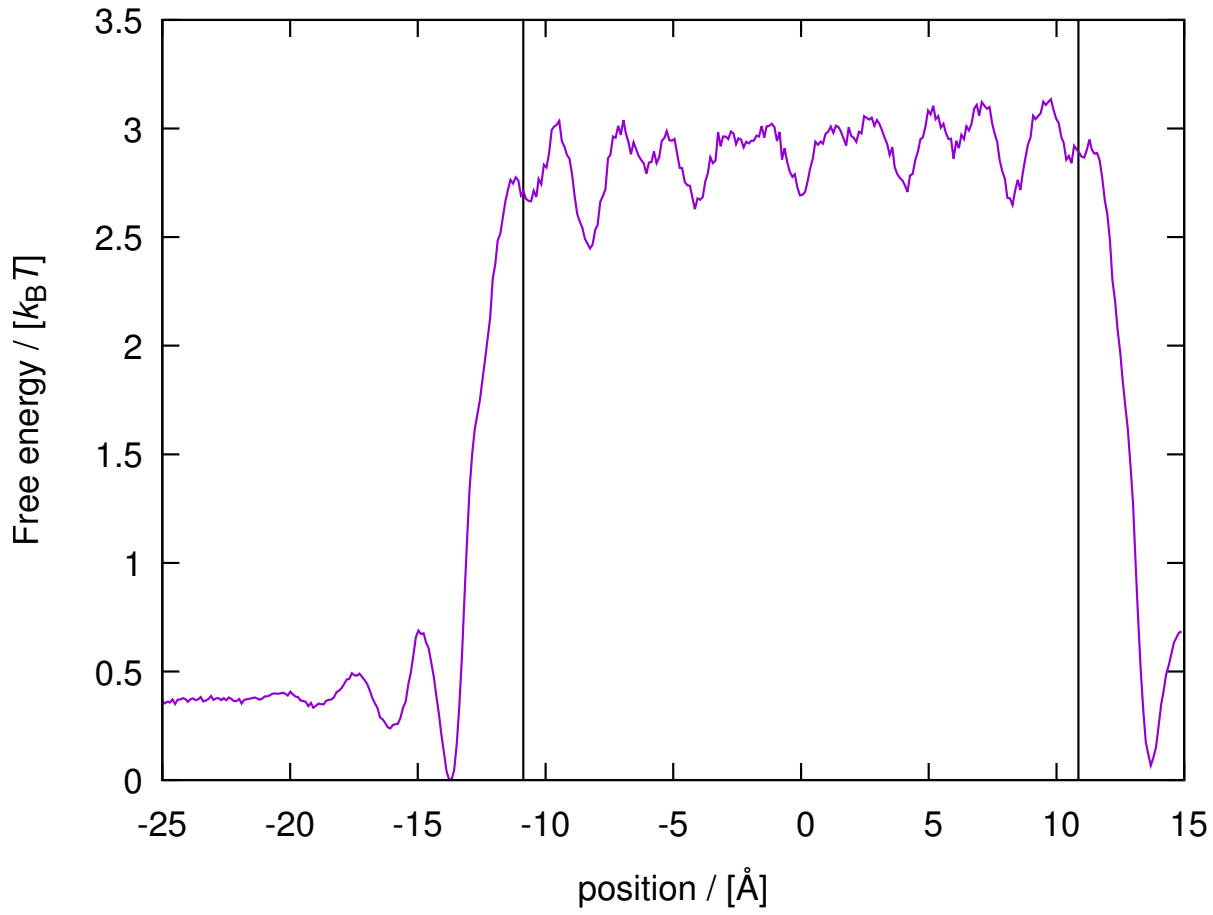

Figure S18: Free energy landscape of water molecules in MRE in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

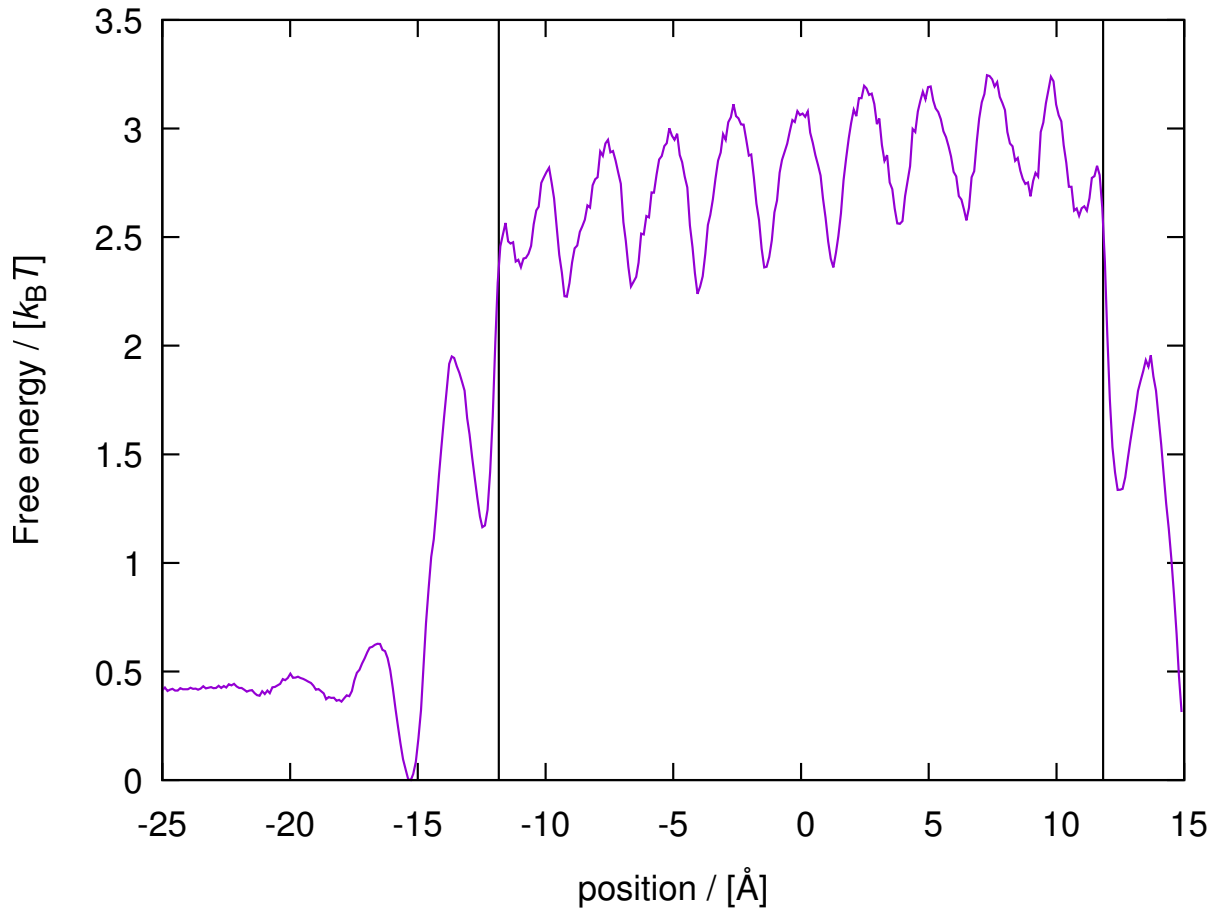

Figure S19: Free energy landscape of water molecules in MTT in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

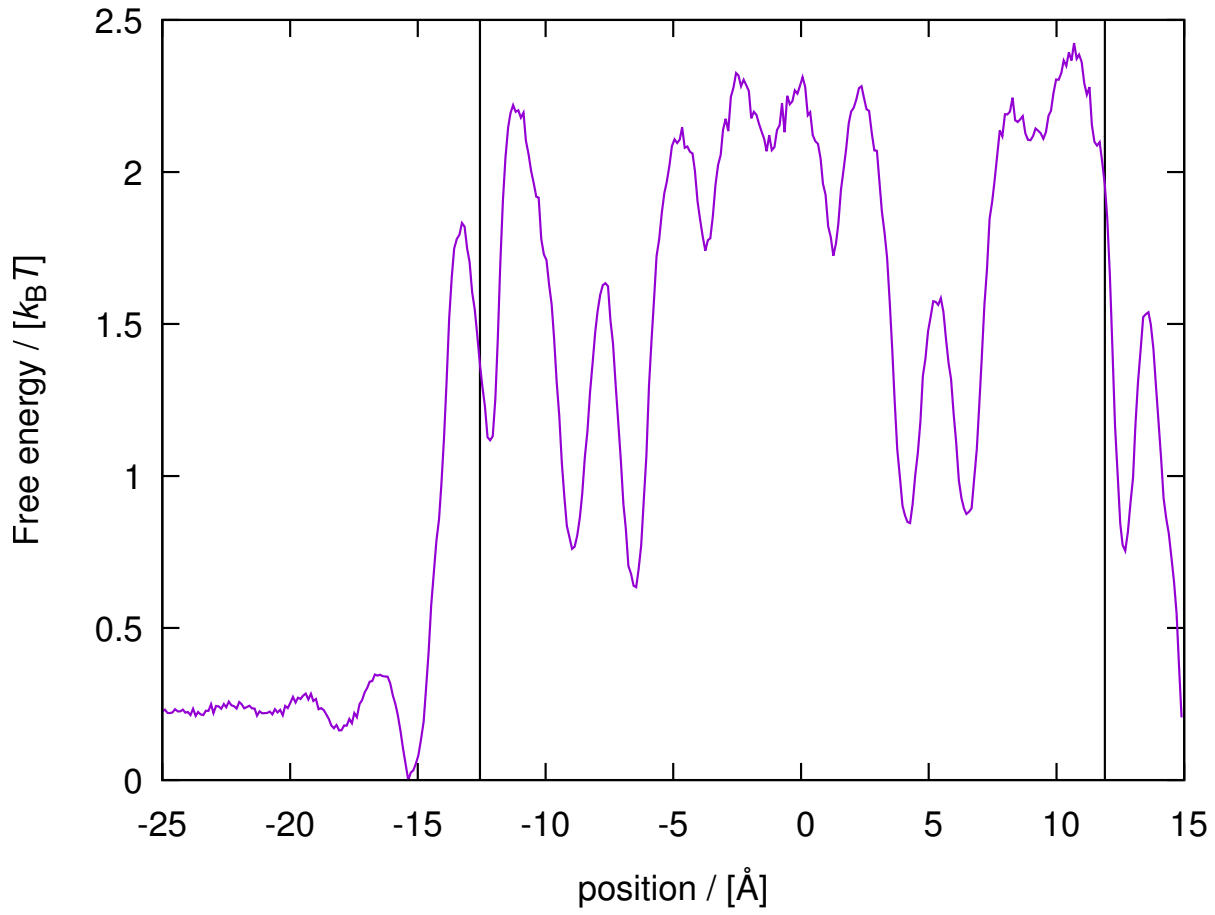

Figure S20: Free energy landscape of water molecules in NES in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

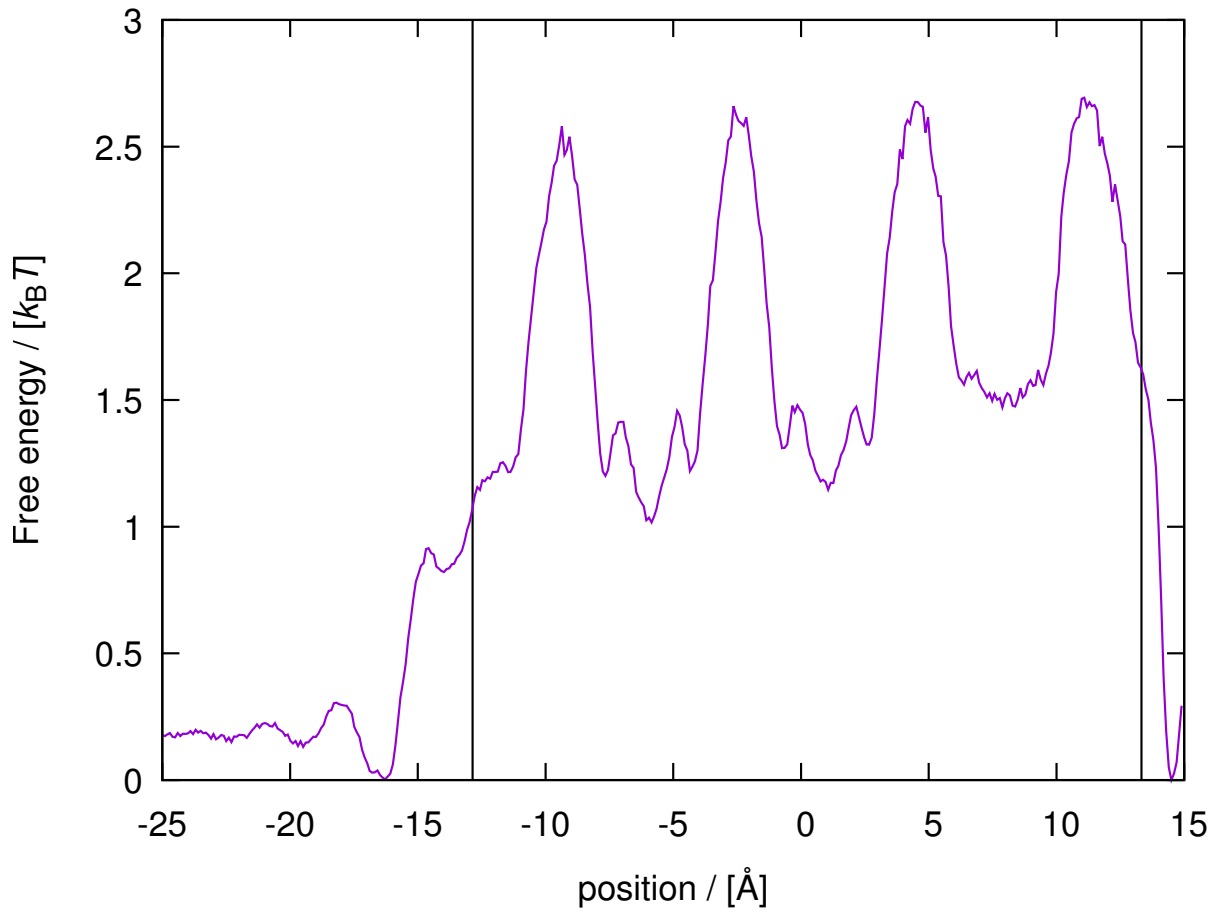

Figure S21: Free energy landscape of water molecules in ATS in the y direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

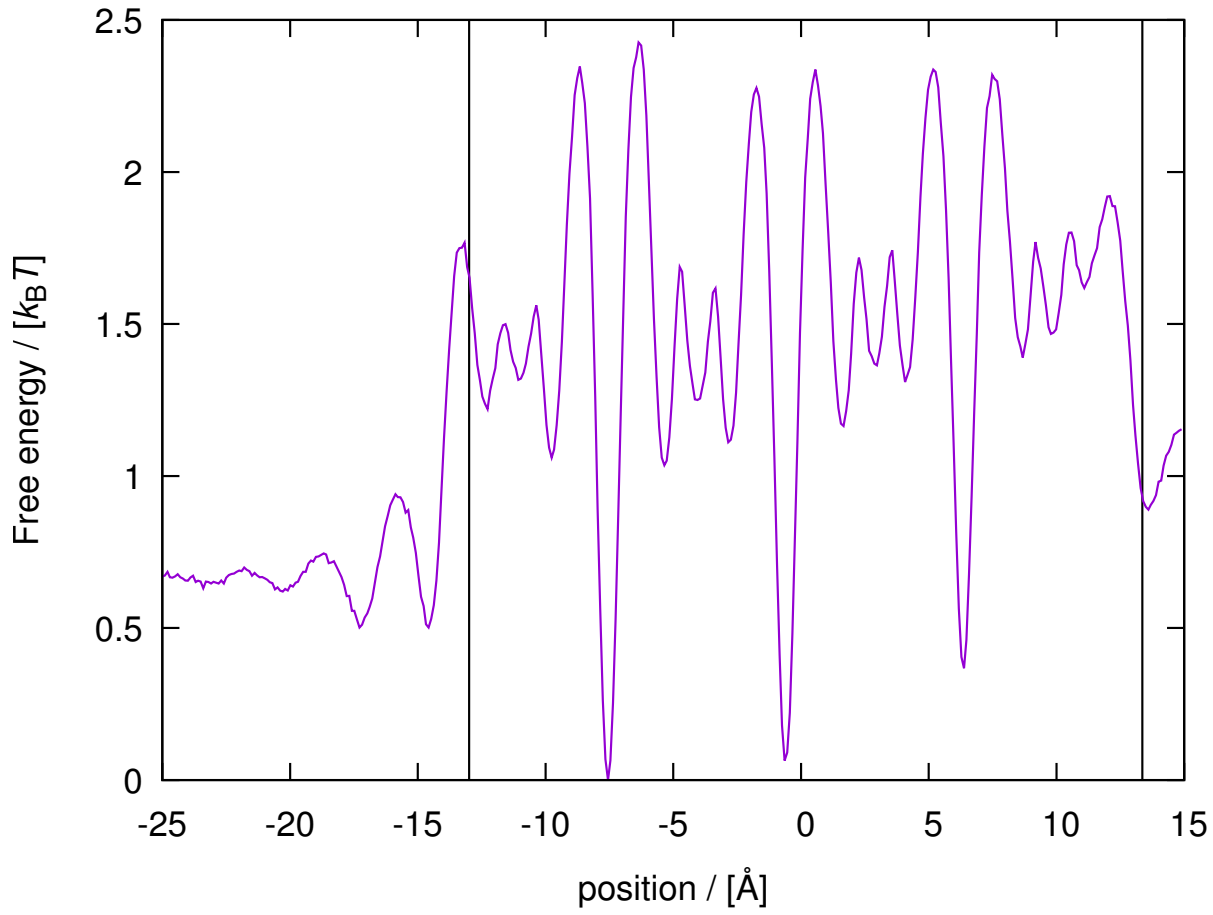

Figure S22: Free energy landscape of water molecules in OBW in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

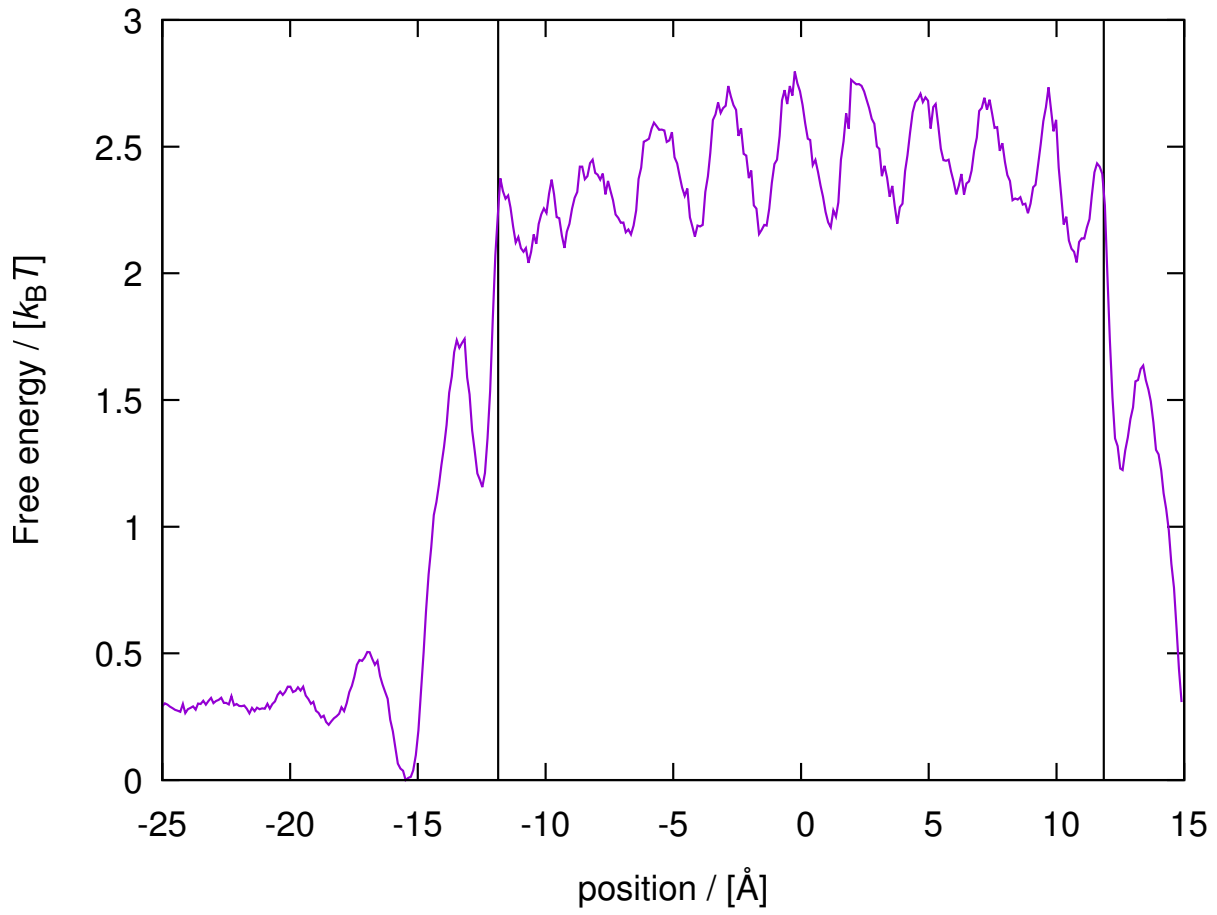

Figure S23: Free energy landscape of water molecules in ATS in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

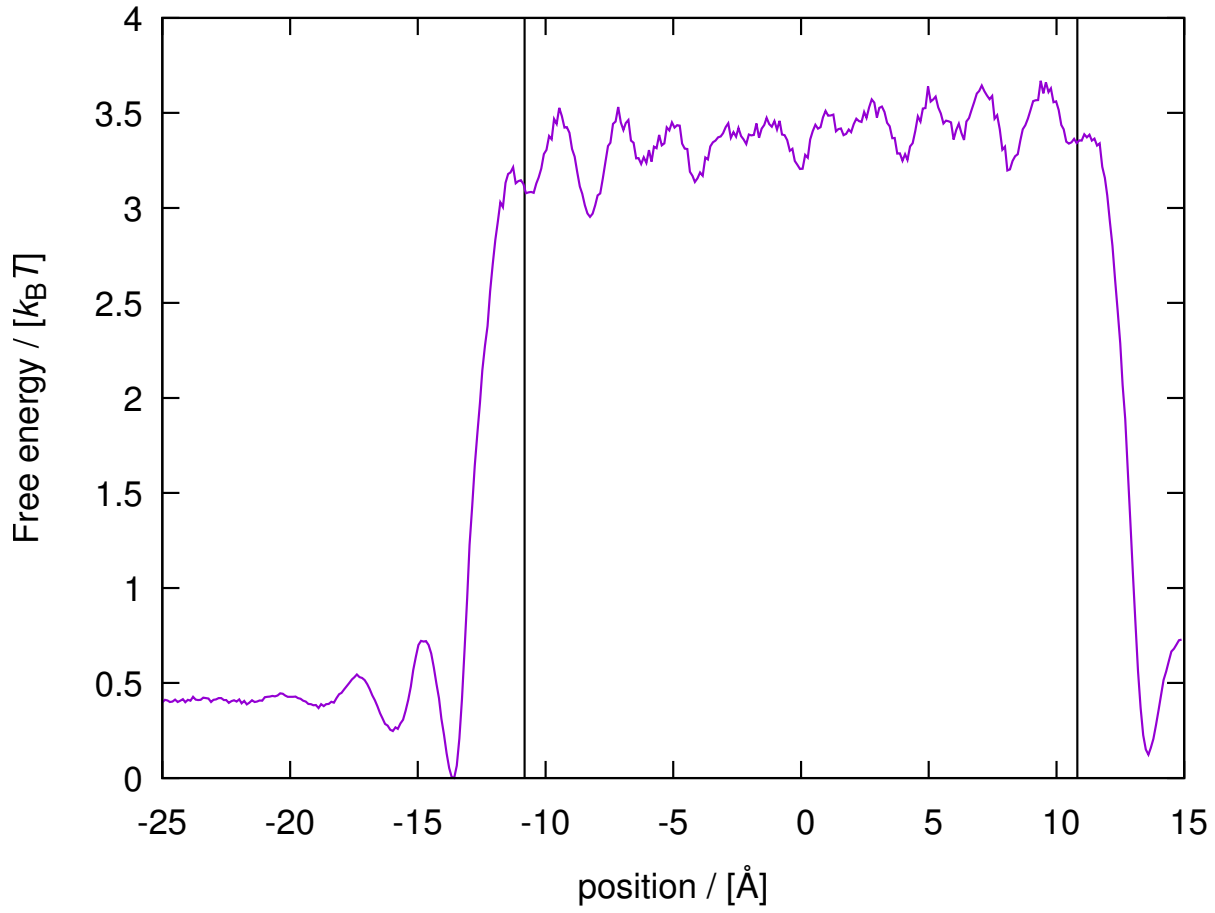

Figure S24: Free energy landscape of water molecules in PSI in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

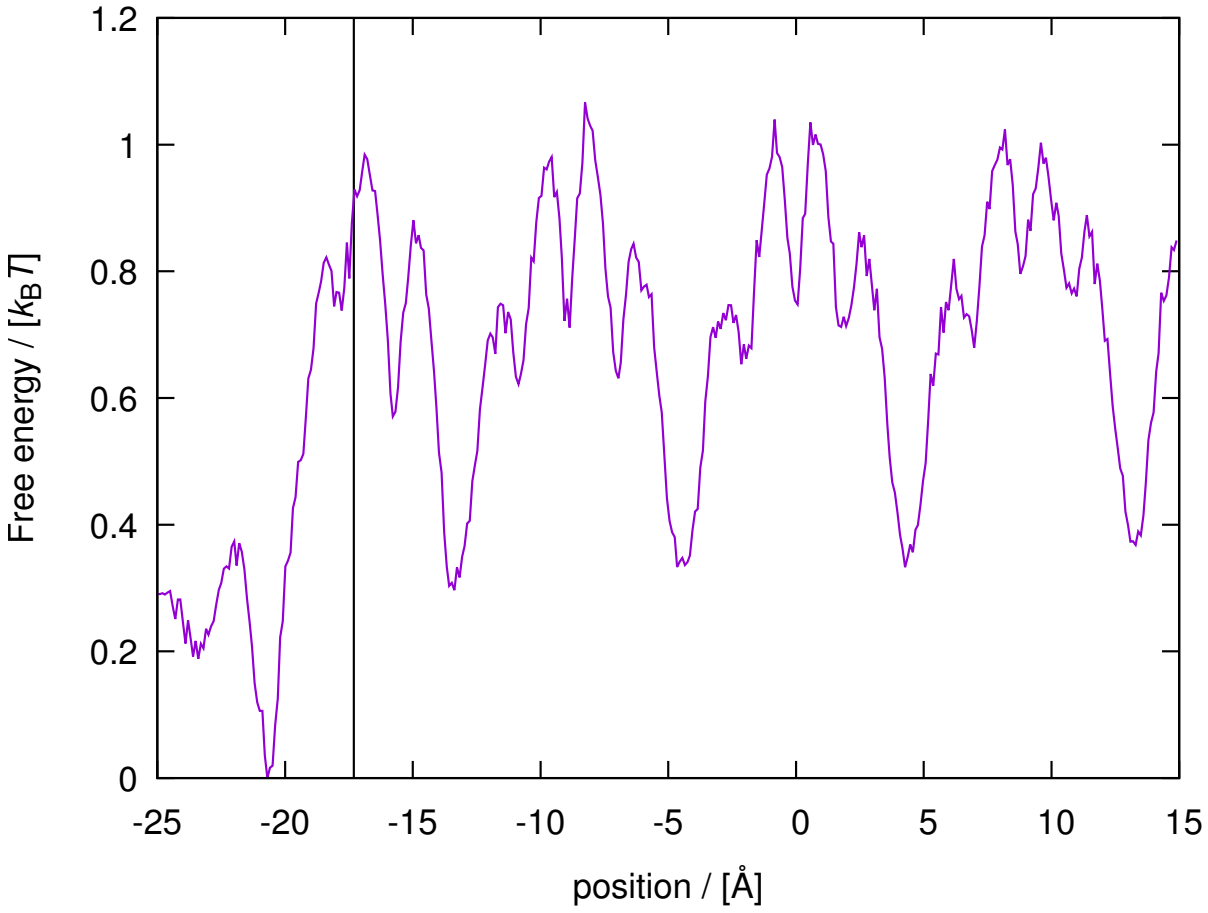

Figure S25: Free energy landscape of water molecules in RWY in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

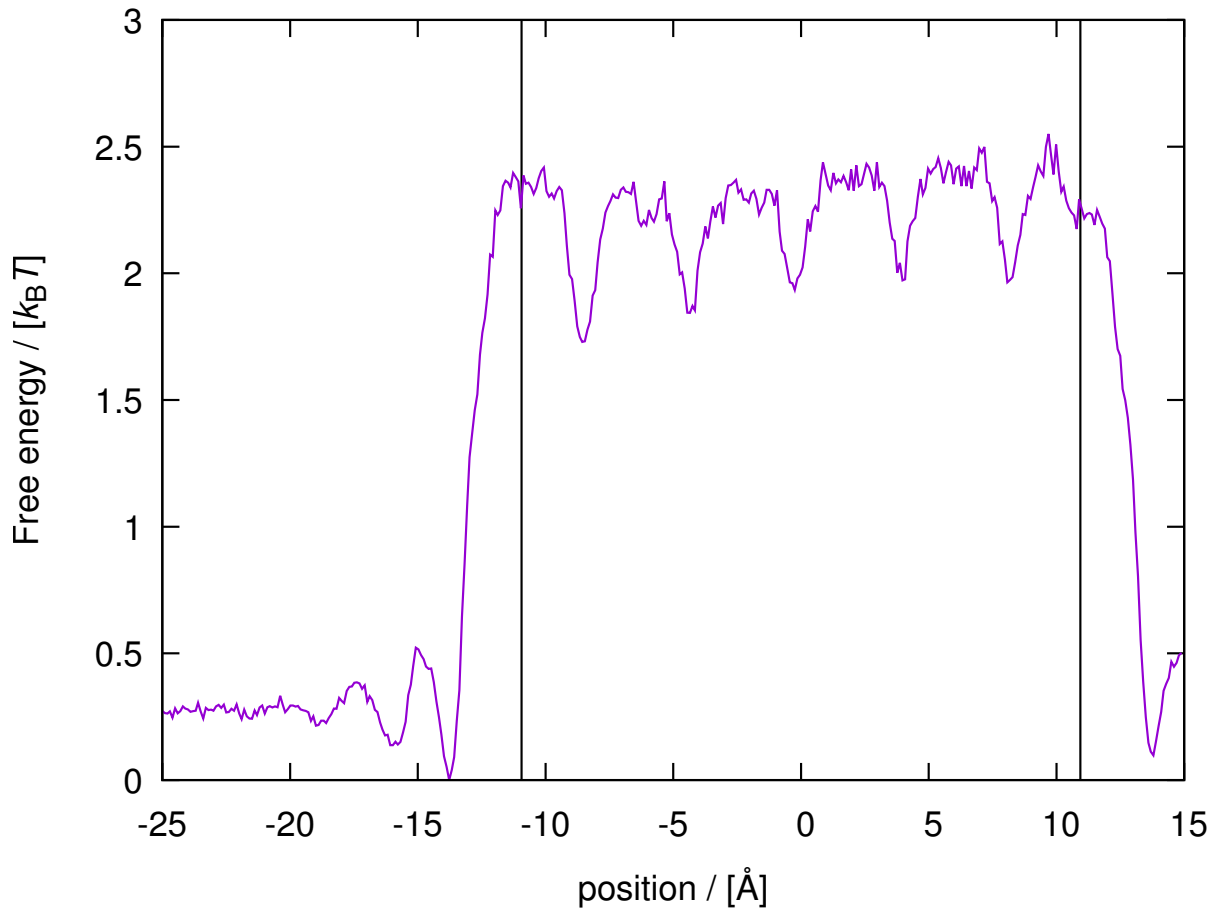

Figure S26: Free energy landscape of water molecules in SAF in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

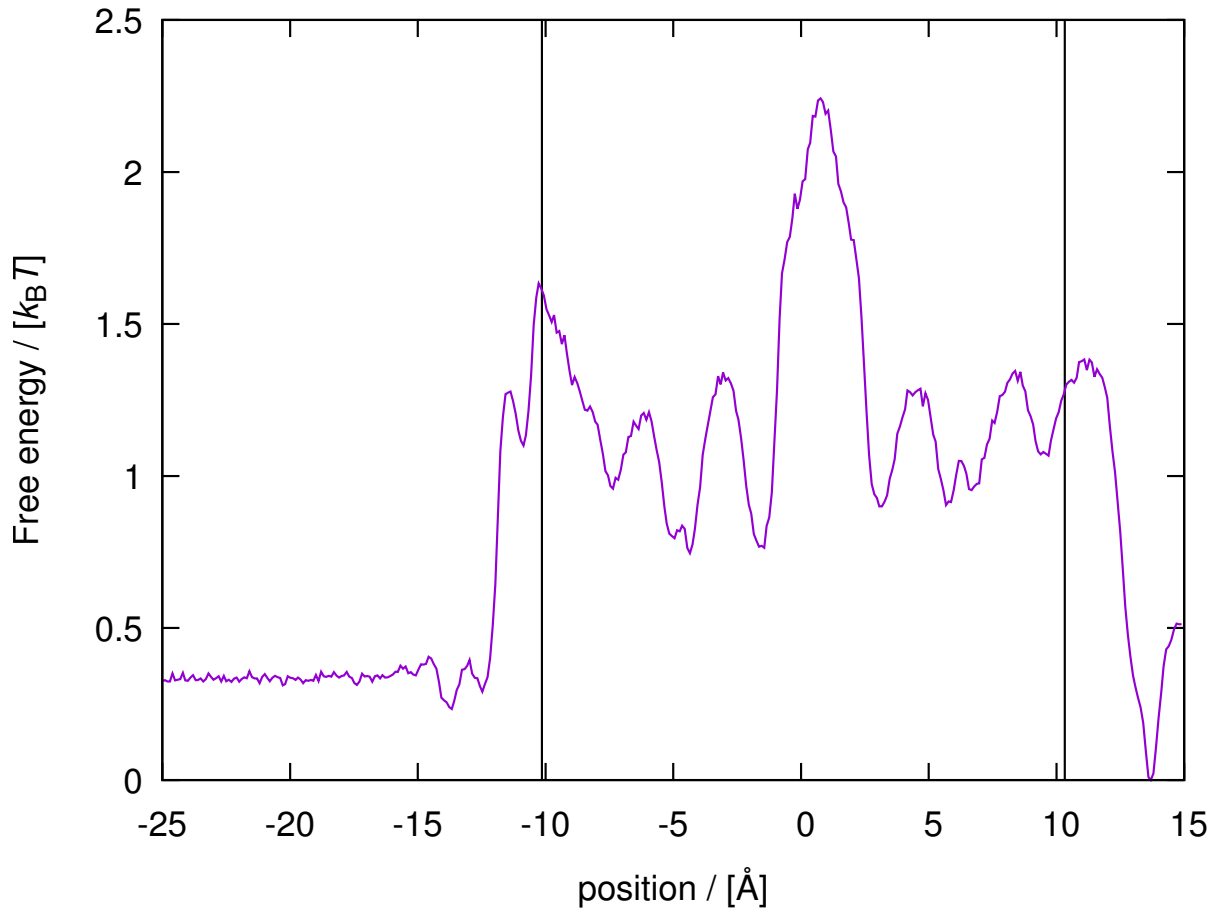

Figure S27: Free energy landscape of water molecules in SAO in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

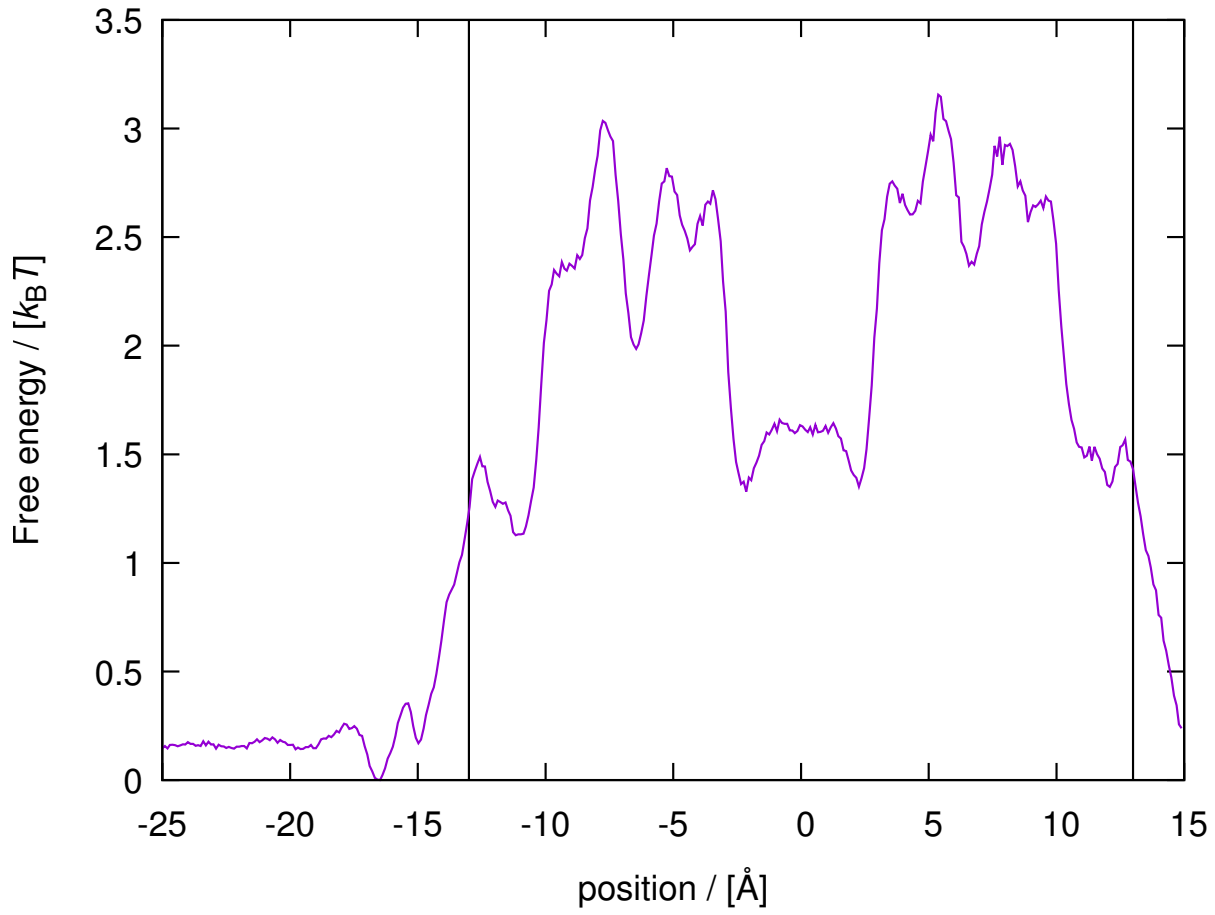

Figure S28: Free energy landscape of water molecules in SFG in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

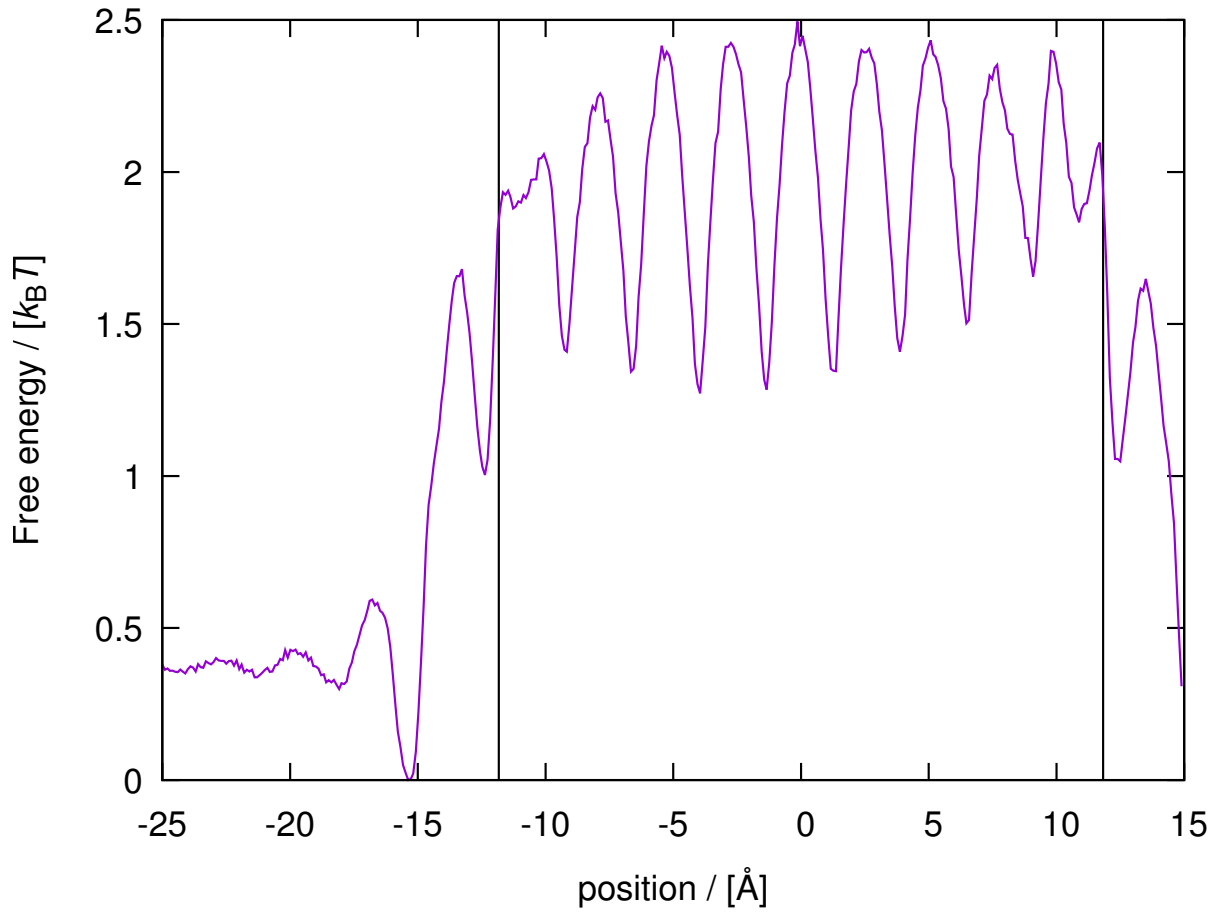

Figure S29: Free energy landscape of water molecules in SSY in the x direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

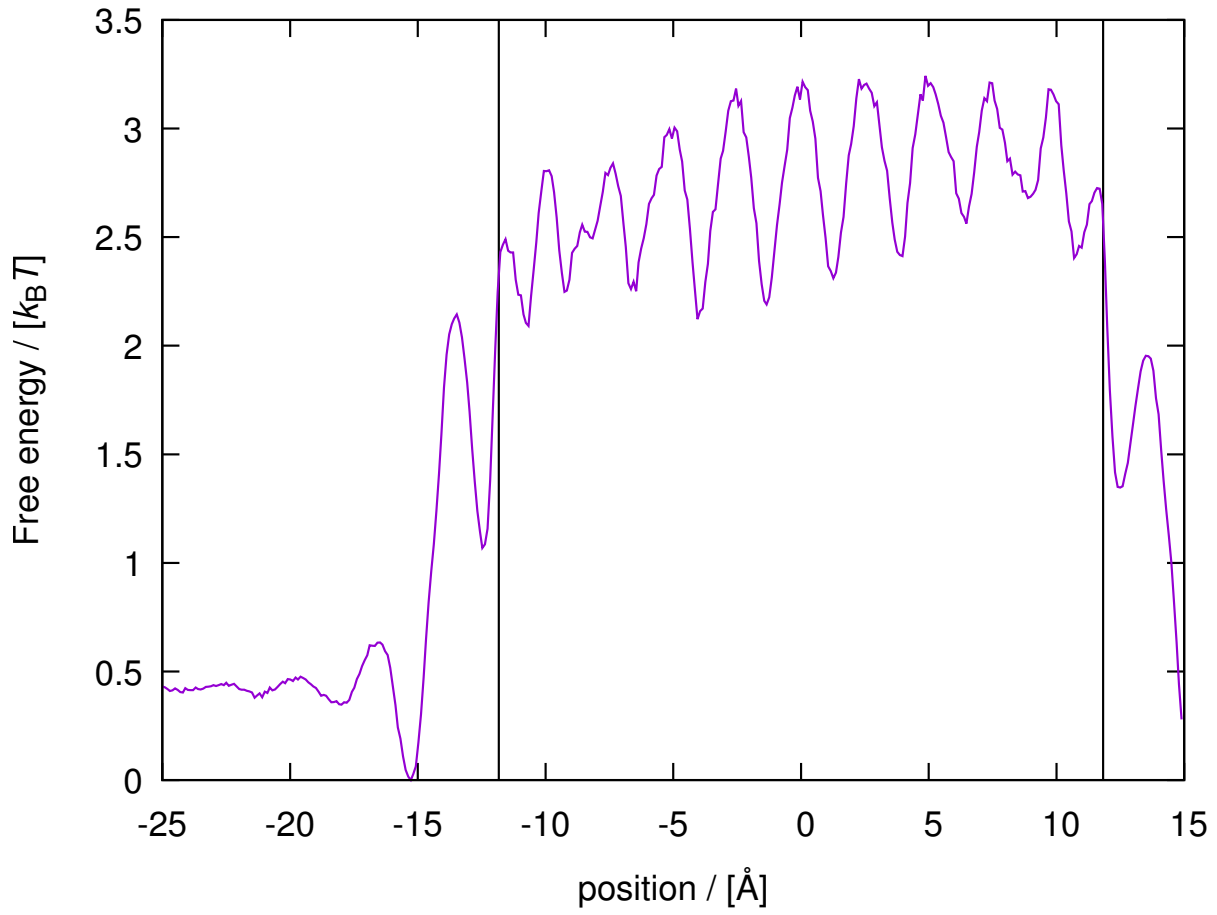

Figure S30: Free energy landscape of water molecules in TON in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

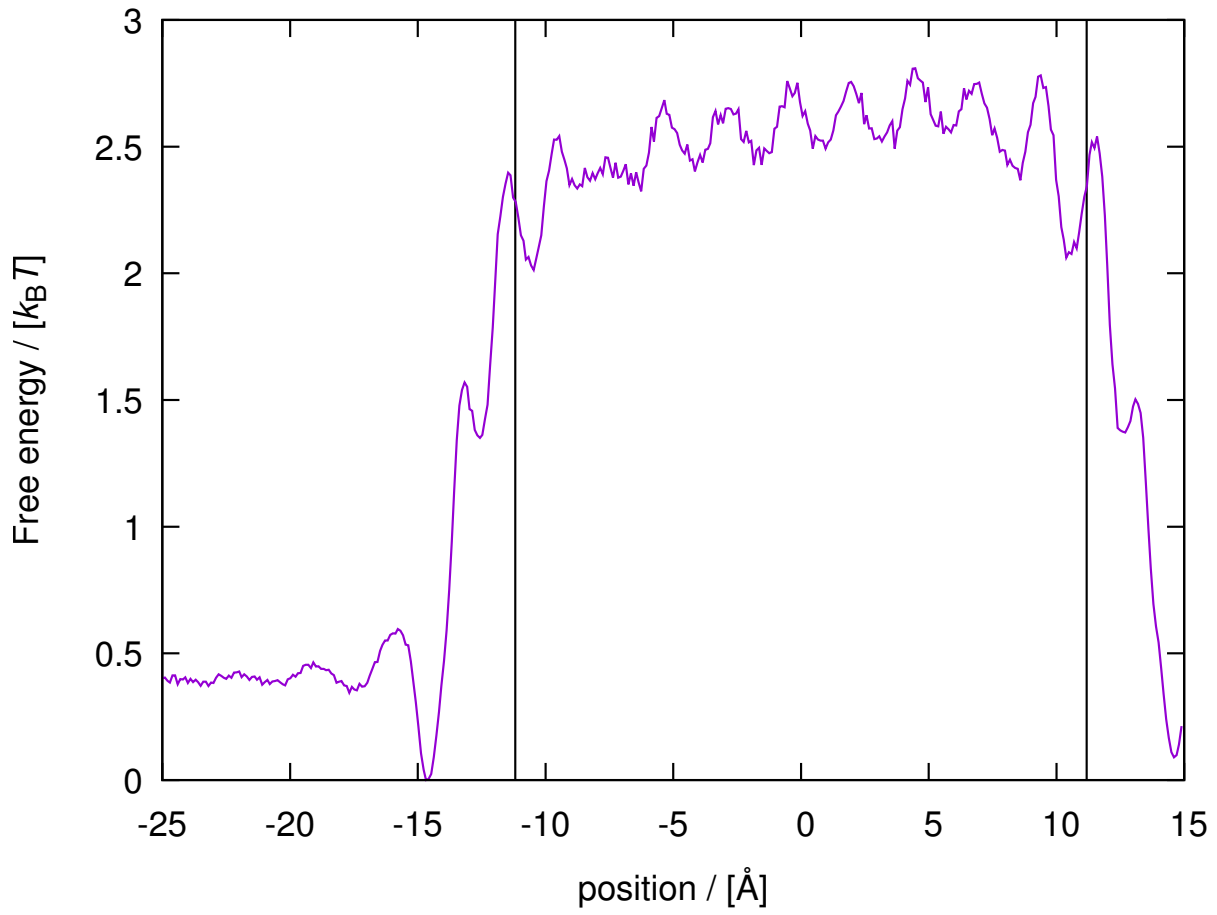

Figure S31: Free energy landscape of water molecules in VET in the z direction. The vertical lines show the boundaries of the zeolite nanosheet membrane, determined by the position of the furthest silicon atoms from the center.

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