Electronic Supporting Information

Diffusion Mechanisms and Preferential Dynamics of Promoter Molecules in ZSM-5 Zeolite†

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Contents

1 Zeolite Lattice Parameters

The MFI structure used in this study is take from the Database of Zeolite Structure.[1]
The lattice parameters are as follows; a: 20.0900 Å, b: 19.7380 Å, c: 13.1420 Å, α: 90°, β: 90°, γ: 90°.

2 Molecular Mechanics Force Field Potentials

What follows are the force field parameters for the simulations described in the main text. All atoms were subject to standard Coulombic interaction potential eq. (1), this was applied directly in the short range and by a particle-particle particle-mesh solver in the long range.[2] Silicon atoms were assigned a charge of +4 and zeolite oxygens a charge of −2; all other charges were assigned according to the OPLS force field scheme.[3,4]

Coulombic:

$$E = \frac{Cq_iq_j}{\varepsilon r} \tag{1}$$

Buckingham:

$$E = Ae^{-r/\rho} - \frac{C}{r^6} \tag{2}$$

Lennard-Jones:

$$E = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3}$$

Bonds:

$$E = K(r - r_0)^2 \tag{4}$$

Angles:

$$E = K(r - \theta_0)^2 \tag{5}$$

Dihedrals:

$$E = \frac{1}{2}K_1[1+\cos(\phi)] + \frac{1}{2}K_3[1+\cos(2\phi)] + \frac{1}{2}K_2[1+\cos(3\phi)] + \frac{1}{2}K_4[1+\cos(4\phi)] \tag{6}$$

Improper:

$$E = K[1 + d\cos(n\phi)] \tag{7}$$

Table 1 Zeolite Buckingham potentials of the form in eq. (2)

Atom 1	Atom 2	A / (kcal mol^{-1})	ρ / Å	C / (kcal mol^{-1}Å^6)
Si	O (zeolite)	29607.6012	0.32052	245.8618956
O (zeolite)	O (zeolite)	524950.3537	0.149	642.928126

Table 2 Lennard-Jones potentials of the form in eq. (3)

Atom 1	Atom 2	ε / (kcal mol^{-1})	σ / Å
O (carbonyl)	O (carbonyl)	0.21	2.96
O (carbonyl)	C (sp^2)	0.1212	3.2416
O (carbonyl)	C (sp^3)	0.1177	3.2187
O (carbonyl)	H-sp^2	0.251	2.7203
O (carbonyl)	H-sp^3	0.251	2.6764
O (carbonyl)	O (ester)	0.1715	2.9298
C (sp^2)	C (sp^2)	0.07	3.55
C (sp^2)	C (sp^3)	0.068	3.5249
C (sp^2)	H-sp^2	0.145	2.9791
C (sp^2)	H-sp^3	0.145	2.931
C (sp^2)	O (ester)	0.099	3.2086
C (sp^3)	C (sp^3)	0.066	3.5
C (sp^3)	H-sp^2	0.1407	2.958
C (sp^3)	H-sp^3	0.1407	2.9103
C (sp^3)	O (ester)	0.0961	3.1859
H-sp^2	H-sp^2	0.3	2.5
H-sp^2	H-sp^3	0.3	2.4597
H-sp^2	O (ester)	0.2049	2.6492
H-sp^3	H-sp^3	0.3	2.42
H-sp^3	O (ester)	0.2049	2.6492
O (ester)	O (ester)	0.14	2.9

Table 3 Lennard-Jones potentials of the form in eq. (3)

Atom 1	Atom 2	ε / (kcal mol^{-1})	σ / Å
O (carbonyl)	Si	0.19442	3.2785
O (carbonyl)	O (zeolite)	0.20494	2.744
C (sp^2)	Si	0.13748	3.6304
C (sp^2)	O (zeolite)	0.14849	3.0959
C (sp^3)	Si	0.13748	3.6304
C (sp^3)	O (zeolite)	0.14849	3.0959
H-sp^2	Si	0	1.6704
H-sp^2	O (zeolite)	0	1.4254
H-sp^3	Si	0	1.6704
H-sp^3	O (zeolite)	0	1.4254
O (ester)	Si	0.19442	3.2785
O (ester)	O (zeolite)	0.20494	2.744

Table 4 Lennard-Jones potentials of the form in eq. (3)

Atom 1	Atom 2	ε / (kcal mol^{-1})	σ / Å
O (carbonyl)	C (methanol)	0.18894	3.03895
C (sp^2)	C (methanol)	0.10909	3.32806
C (sp^3)	C (methanol)	0.10592	3.30454
H-sp^2	C (methanol)	0.07141	2.79285
H-sp^3	C (methanol)	0.07141	2.7478
O (ester)	C (methanol)	0.15427	3.00799
Si	C (methanol)	0.13748	3.6304
O (zeolite)	C (methanol)	0.14849	3.0959
C (methanol)	C (methanol)	0.17	3.12
C (methanol)	H (methanol)	0	0
O (carbonyl)	H (methanol)	0	0
C (sp^2)	H (methanol)	0	0
C (sp^3)	H (methanol)	0	0
H-sp^2	H (methanol)	0	0
H-sp^3	H (methanol)	0	0
O (ester)	H (methanol)	0	0
Si	H (methanol)	0	0
O (zeolite)	H (methanol)	0	0

Table 5 Bond potentials of the form in eq. (4)

Atom 1	Atom 2	K / (kcal mol^{-1})	r_0 / Å
C (sp^2)	O (aldehyde)	570	1.229
C (aldehyde)	C (sp^2)	400	1.49
C (sp^2)	C (sp^2)	469	1.4
C (sp^2)	C (sp^3)	317	1.51
C (sp^3)	C (sp^3)	268	1.529
C (sp^3)	H-sp^3	340	1.09
C (sp^2)	H-sp^2	367	1.08
C (methanol)	O (methanol)	320	1.41
O (methanol)	H-O (methanol)	553	0.945

Table 6 Angle potentials of the form in eq. (5)

Atom 1	Atom 2	Atom 3	K / (kcal mol^{-1})	θ_0 / Å
C (sp^2)	C (sp^2)	H-sp^2	35	120
O (aldehyde)	C (sp^2)	H-sp^2	35	123
C (sp^3)	C (sp^3)	H-sp^3	37.5	110.7
C (sp^3)	C (sp^3)	C (sp^3)	58.35	112.7
C (sp^2)	C (sp^3)	C (sp^3)	63	114
C (sp^2)	C (sp^2)	C (sp^2)	63	120
C (sp^2)	C (sp^2)	C (sp^3)	70	120
O(aldehyde)	C (aldehyde)	C (sp^2)	80	120.4
C (aldehyde)	C (sp^2)	C (sp^2)	85	120
C (sp^2)	C (sp^3)	H-sp^3	35	109.5
H-sp^3	C (sp^3)	H-sp^3	33	107.8
C (sp^2)	C (aldehyde)	H (aldehyde)	35	115
C (methanol)	O (methanol)	H-O (methanol)	55	108.5

Table 7 Dihedral potentials of the form in eq. (6); values for K_n are given in units of (kcal mol^{-1}).

Atom 1	Atom 2	Atom 3	Atom 4	K_1	K_2	K_3	K_4
C (sp^3)	C (sp^3)	C (sp^2)	C (sp^2)	0	0	0	0
H-sp^3	C (sp^3)	C (sp^3)	C (sp^3)	0	0	0.3	0
H-sp^3	C (sp^3)	C (sp^3)	C (sp^2)	0	0	0.462	0
H (aldehyde)	C (aldehyde)	C (sp^2)	C (sp^2)	0	0.2	0	0
C (sp^2)	C (sp^2)	C (aldehyde)	O (aldehyde)	0	2.1	0	0
H-sp^2	C (sp^2)	C (sp^2)	C (sp^2)	0	7.25	0	0
C (sp^3)	C (sp^3)	C (sp^3)	C (sp^2)	1.3	-0.2	0.2	0
H-O (methanol)	O (methanol)	C (methanol)	H (methanol)	0	0	0.352	0

Table 8 Improper potentials of the form in eq. (7)

Atom 1	Atom 2	Atom 3	Atom 4	K / (kcal mol^{-1})	d	n
C (sp^2)	H-sp^2	C (sp^2)	C (sp^2)	0	-1	2
C (sp^2)	C (sp^2)	C (sp^2)	C (sp^3)	2.5	-1	2
O (aldehyde)	C (aldehyde)	C (sp^2)	H (aldehyde)	10.5	-1	2

3 MSD plots

The plots in this section show the mean squared displacement of the centre-of-mass of the molecules listed. The black line in each plot is the ensemble average of 80 promoter molecules or 160 methanol molecules. The vertical green line on each plot shows the point from which the diffuse regime is assumed; all data after this point is used in estimating diffusion coefficients. From darkest to lightest, the blue-shaded regions show the 68^{th}, 97.5^{th}, and the 99.7^{th} percentiles.

3.1 Aliphatic ester promoters

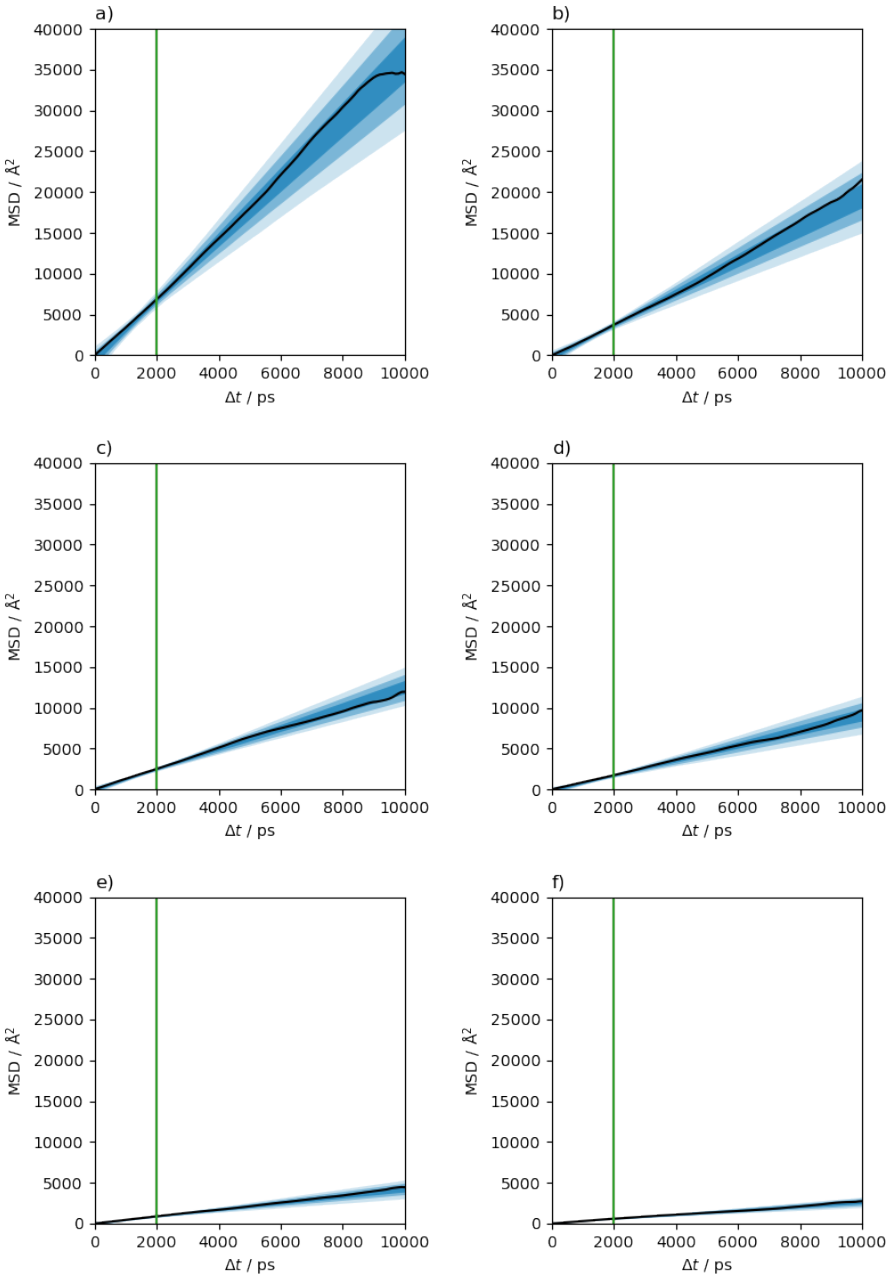

Figure 1 Aliphatic ester promoters without methanol: a) methyl formate b) methyl acetate c) methyl propionate d) methyl butyrate e) methyl pentanoate f) methyl hexanoate

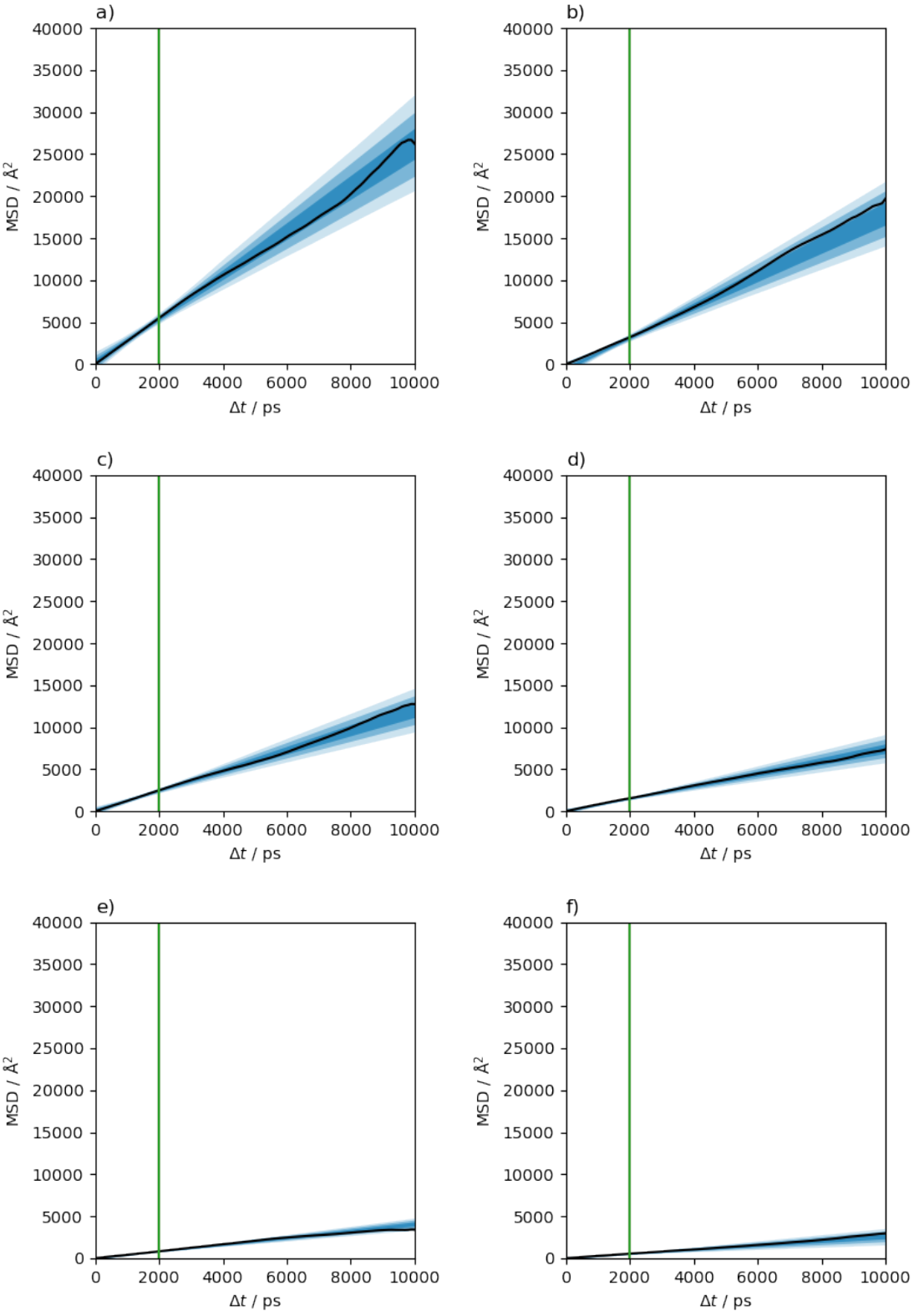

Figure 2 Aliphatic ester promoters with methanol: a) methyl formate b) methyl acetate c) methyl propionate d) methyl butyrate e) methyl pentanoate f) methyl hexanoate

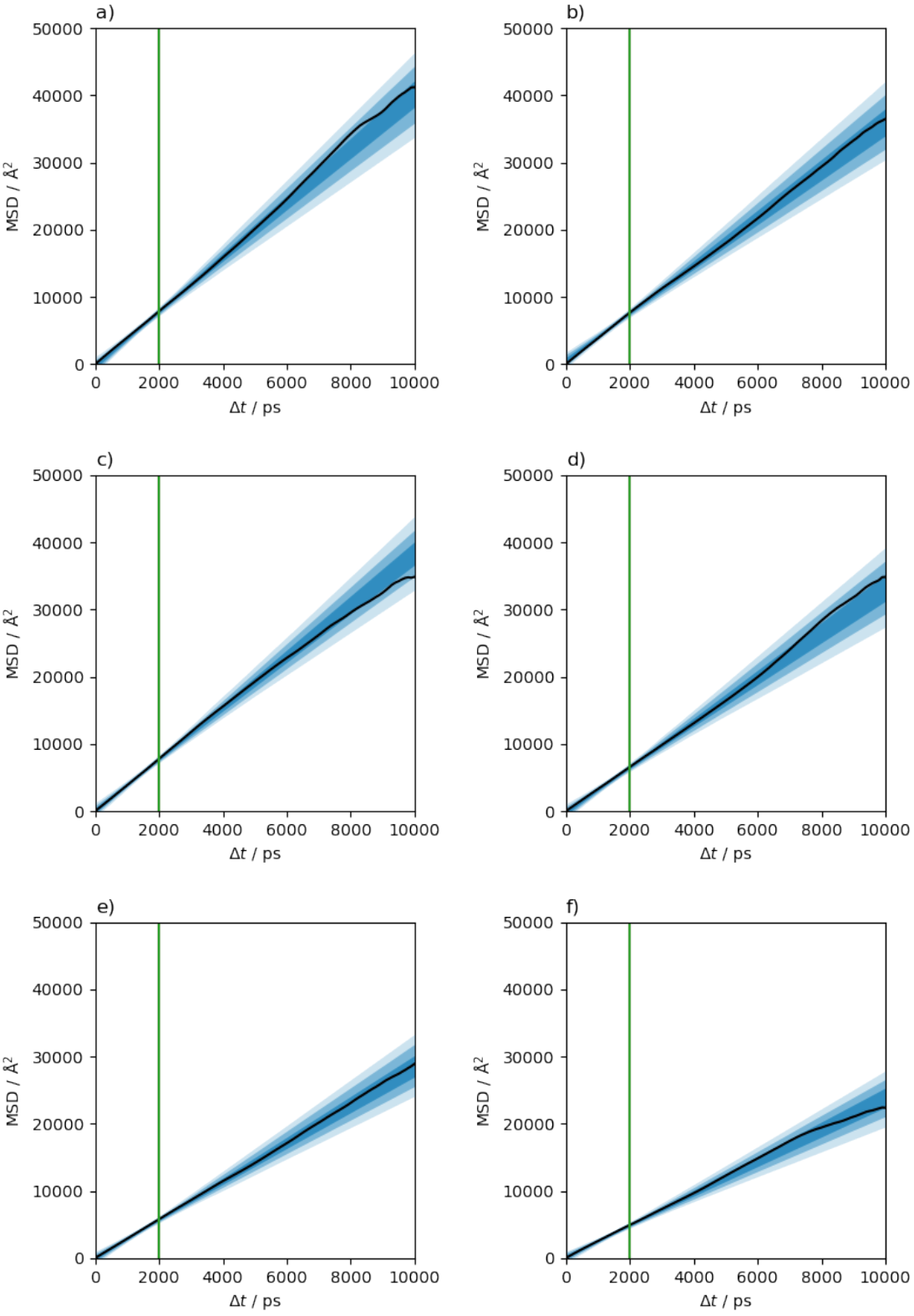

Figure 3 Methanol with aliphatic ester promoters: a) methyl formate b) methyl acetate c) methyl propionate d) methyl butyrate e) methyl pentanoate f) methyl hexanoate

3.2 Aromatic aldehyde promoters

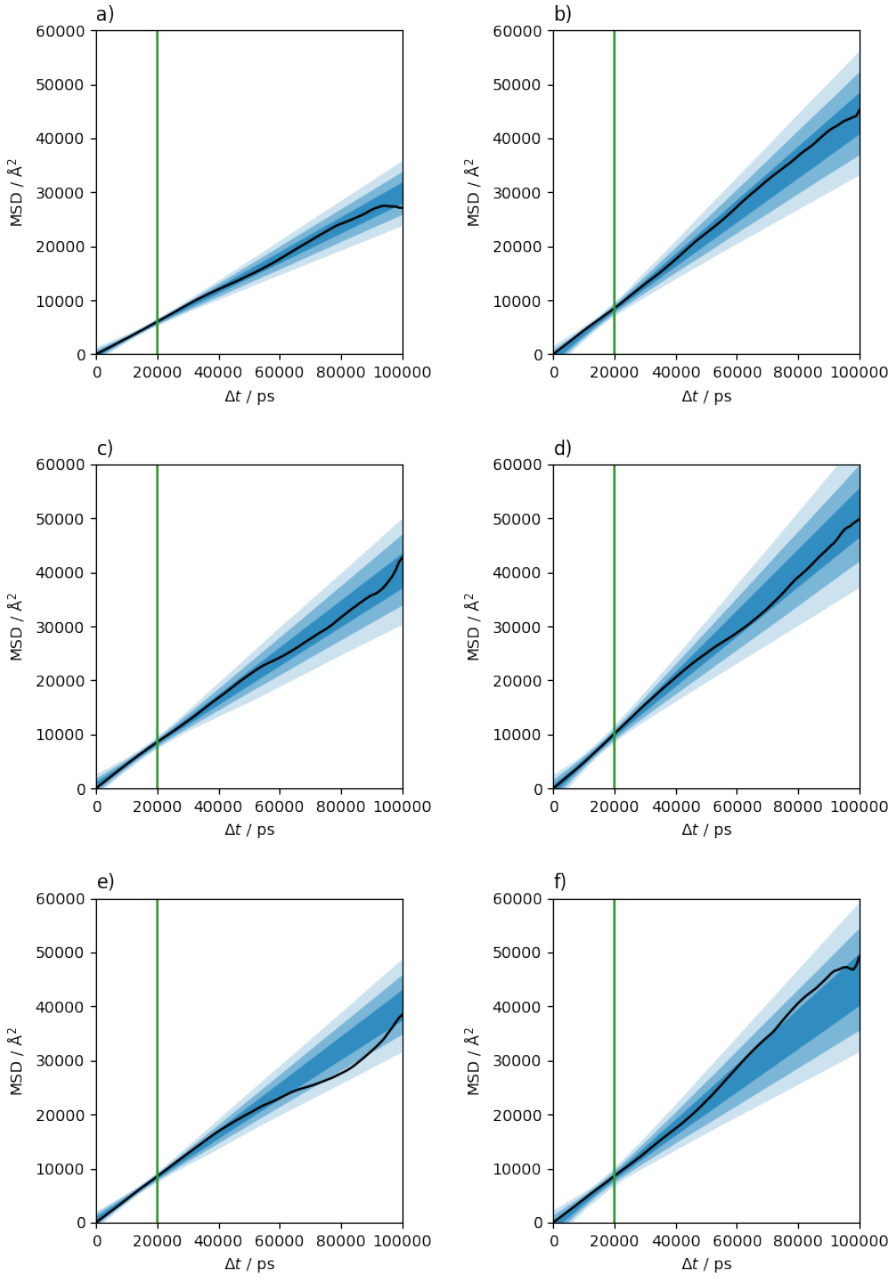

Figure 4 Aromatic aldehyde promoters without methanol: a) benzaldehyde b) 4-methyl benzaldehyde c) 4-ethyl benzaldehyde d) 4-*n*-propyl benzaldehyde e) 4-*n*-butyl benzaldehyde f) 4-*n*-pentyl benzaldehyde

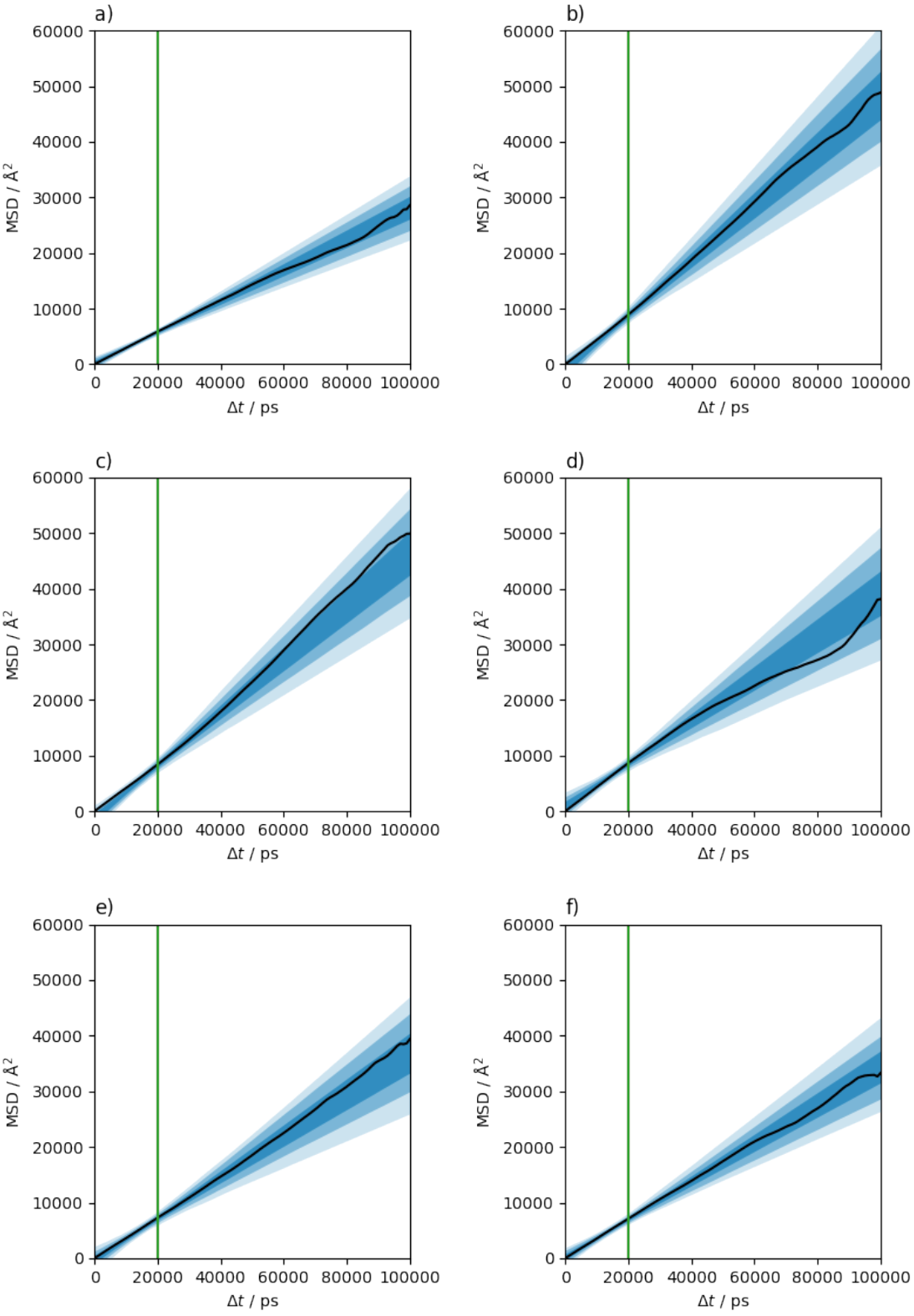

Figure 5 Aromatic aldehyde promoters with methanol: a) benzaldehyde b) 4-methyl benzaldehyde c) 4-ethyl benzaldehyde d) 4-*n*-propyl benzaldehyde e) 4-*n*-butyl benzaldehyde f) 4-*n*-pentyl benzaldehyde

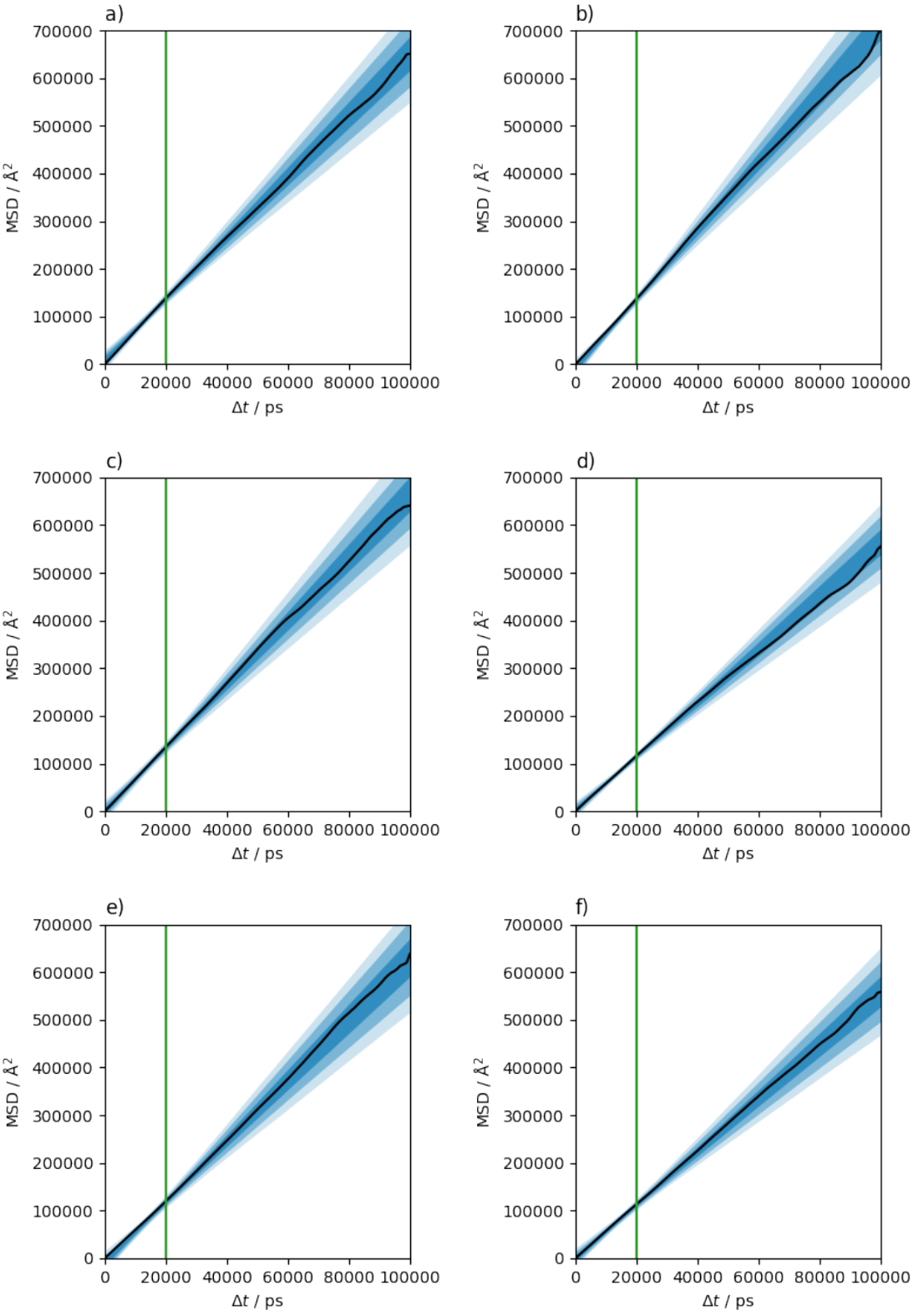

Figure 6 Methanol with aromatic aldehyde promoters: a) benzaldehyde b) 4-methyl benzaldehyde c) 4-ethyl benzaldehyde d) 4-*n*-propyl benzaldehyde e) 4-*n*-butyl benzaldehyde f) 4-*n*-pentyl benzaldehyde

4 Spatial Probability Distribution

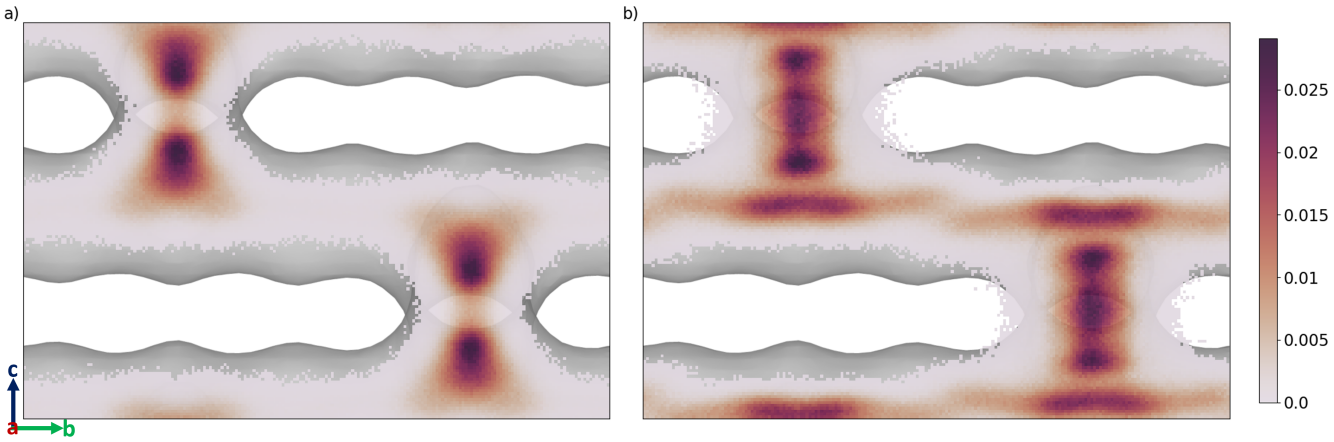

Figure 7 Spatial probability distribution of the molecular centre of mass, in *b* and *c*, of a) benzaldehyde and b) 4-*n*-pentyl benzaldehyde, overlaid on the internal surface of ZSM-5 (Ovito was used to produce this surface with the Gaussian density method[5]).

5 Thermostat tests

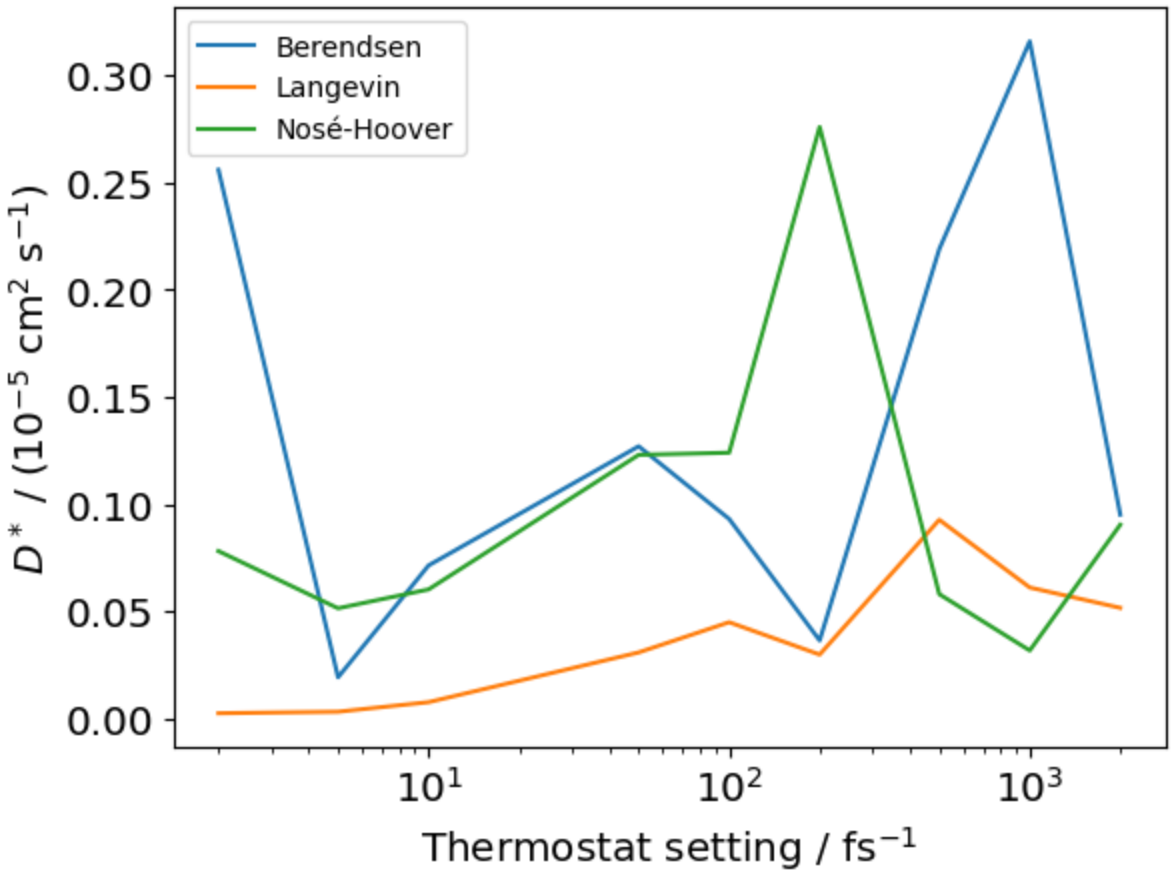

Figure 8 Diffusion coefficients of 4-*n*-pentyl benzaldehyde calculated from simulations with different thermostats and thermostat settings.

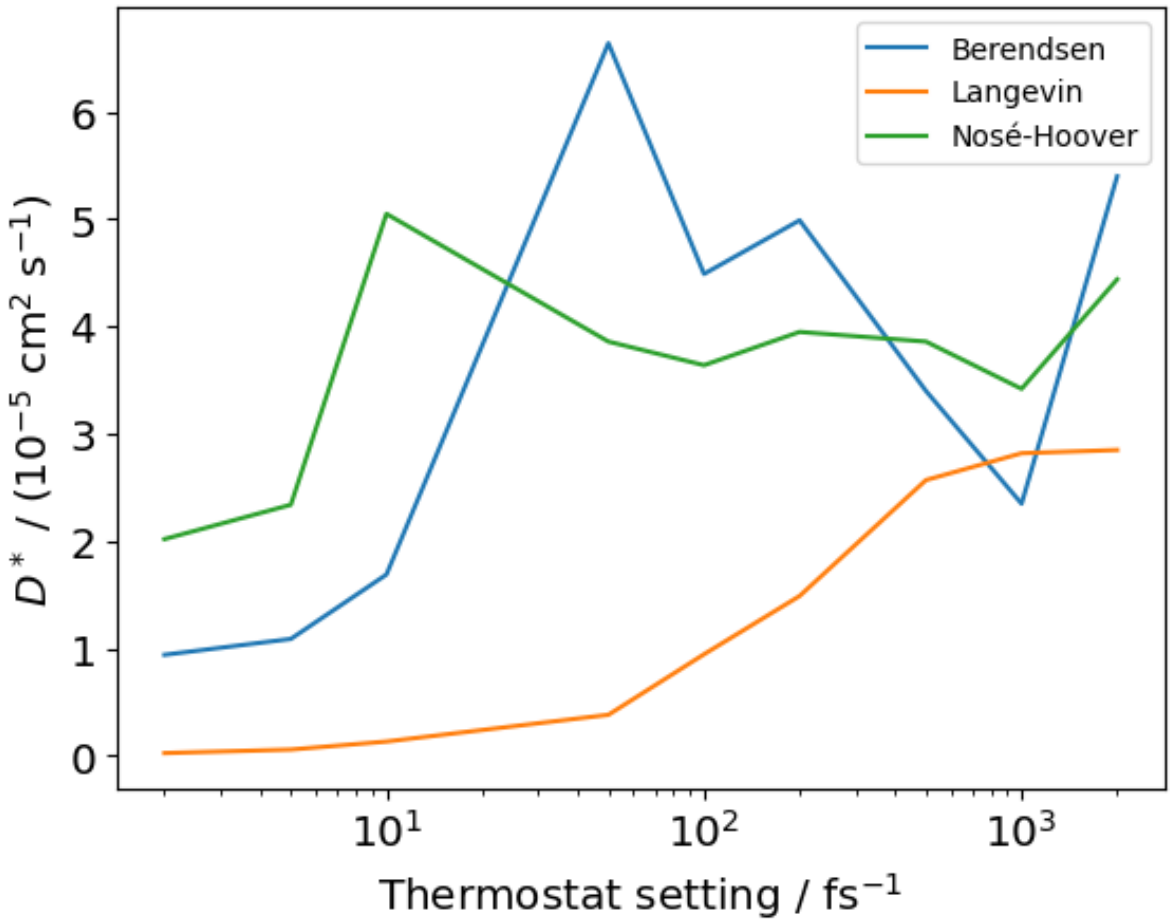

Figure 9 Diffusion coefficients of methanol in the presence of 4-*n*-pentyl benzaldehyde calculated from simulations with different thermostats and thermostat settings.

References

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