Supporting Information: Importance Sampling within Configuration Space Integration for Adsorbate Thermophysical Properties: a case study for CH_3/Ni(111)

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Rigid body hessians

Rigid body hessians were calculated for the two binding positions of methyl and were used to describe the covariance when generating the gaussian training geometries. These matracies

are:

$$H_{fcc} = \begin{bmatrix} 3.43e+00 & 5.44e-03 & -3.71e-02 & -2.24e-01 & -3.85e-01 & 1.00e-02 \\ 5.44e-03 & 3.43e+00 & -4.76e-03 & 3.74e-01 & -2.17e-01 & 2.07e-02 \\ -3.71e-02 & -4.76e-03 & 8.55e+00 & -1.33e-02 & -1.48e-03 & -1.22e-02 \\ -2.24e-01 & 3.74e-01 & -1.33e-02 & 2.12e+00 & 1.21e-03 & 8.46e-03 \\ -3.85e-01 & -2.17e-01 & -1.48e-03 & 1.21e-03 & 2.10e+00 & -1.01e-02 \\ 1.00e-02 & 2.07e-02 & -1.22e-02 & 8.46e-03 & -1.01e-02 & 2.02e+00 \end{bmatrix}$$

$$H_{hcp} = \begin{bmatrix} 2.83e+00 & 2.04e-03 & 1.12e-02 & -3.56e-01 & -6.66e-03 & -7.40e-04 \\ 2.04e-03 & 2.85e+00 & 3.30e-02 & 8.52e-03 & -3.49e-01 & -1.85e-03 \\ 1.12e-02 & 3.30e-02 & 6.92e+00 & -2.07e-02 & -1.96e-02 & 3.33e-03 \\ -3.56e-01 & 8.52e-03 & -2.07e-02 & 2.05e+00 & 1.21e-03 & 4.03e-04 \\ -6.66e-03 & -3.49e-01 & -1.96e-02 & 1.21e-03 & 2.02e+00 & 1.62e-03 \\ -7.40e-04 & -1.85e-03 & 3.33e-03 & 4.03e-04 & 1.61e-03 & 1.93e+00 \end{bmatrix}$$

Vibrational frequencies

Table S1: After diagonalization of the full 3N hessians for both binding sites the following vibrational frequencies were found and used in calculating the partition functions for the internal modes.

	Frequency cm^{-1}	
Mode number	fcc	hcp
1	1168.5	1140.0
2	1282.5	1288.7
3	1287.9	1289.9
4	2752.9	2769.7
5	2821.1	2836.6
6	2821.8	2837.2

Coordinates of the minima

Table S2: Positions of atoms for the fcc binding site

	Positions		
Atom type	x	y	z
Ni	0.00	0.00	-6.04
Ni	2.47	0.00	-6.04
Ni	4.94	0.00	-6.04
Ni	1.23	2.14	-6.04
Ni	3.70	2.14	-6.04
Ni	6.17	2.14	-6.04
Ni	2.47	4.27	-6.04
Ni	4.94	4.27	-6.04
Ni	7.40	4.27	-6.04
Ni	1.23	0.71	-4.03
Ni	3.70	0.712	-4.03

Ni	6.17	0.712	-4.03
Ni	2.47	2.85	-4.03
Ni	4.94	2.85	-4.03
Ni	7.40	2.85	-4.03
Ni	3.70	4.99	-4.03
Ni	6.17	4.99	-4.03
Ni	8.64	4.99	-4.03
Ni	0.00	1.42	-2.01
Ni	2.47	1.42	-2.01
Ni	4.94	1.42	-2.01
Ni	1.23	3.56	-2.01
Ni	3.70	3.56	-2.01
Ni	6.17	3.56	-2.01
Ni	2.47	5.70	-2.01
Ni	4.94	5.70	-2.01
Ni	7.40	5.70	-2.01
Ni	0.00	0.00	0.00
Ni	2.47	0.00	0.00
Ni	4.94	0.00	0.00
Ni	1.23	2.14	0.00
Ni	3.70	2.14	0.00
Ni	6.17	2.14	0.00
Ni	2.47	4.27	0.00
Ni	4.94	4.27	0.00
Ni	7.40	4.27	0.00
C	1.23	0.71	1.54
H	1.23	1.75	1.96

H	2.13	0.20	1.96
H	0.34	0.20	1.96

Table S3: Positions of atoms for the hcp binding site

	Positions		
Atom type	x	y	z
Ni	0.00	0.00	-6.04
Ni	2.47	0.00	-6.04
Ni	4.94	0.00	-6.04
Ni	1.23	2.14	-6.04
Ni	3.70	2.14	-6.04
Ni	6.17	2.14	-6.04
Ni	2.47	4.27	-6.04
Ni	4.94	4.27	-6.04
Ni	7.40	4.27	-6.04
Ni	1.23	0.71	-4.03
Ni	3.70	0.712	-4.03
Ni	6.17	0.712	-4.03
Ni	2.47	2.85	-4.03
Ni	4.94	2.85	-4.03
Ni	7.40	2.85	-4.03
Ni	3.70	4.99	-4.03
Ni	6.17	4.99	-4.03
Ni	8.64	4.99	-4.03
Ni	0.00	1.42	-2.01
Ni	2.47	1.42	-2.01

Ni	4.94	1.42	-2.01
Ni	1.23	3.56	-2.01
Ni	3.70	3.56	-2.01
Ni	6.17	3.56	-2.01
Ni	2.47	5.70	-2.01
Ni	4.94	5.70	-2.01
Ni	7.40	5.70	-2.01
Ni	0.00	0.00	0.00
Ni	2.47	0.00	0.00
Ni	4.94	0.00	0.00
Ni	1.23	2.14	0.00
Ni	3.70	2.14	0.00
Ni	6.17	2.14	0.00
Ni	2.47	4.27	0.00
Ni	4.94	4.27	0.00
Ni	7.40	4.27	0.00
C	2.47	1.42	1.56
H	1.57	1.94	1.98
H	3.36	1.94	1.98
H	2.47	0.392	1.99

Convergence data

Maybe we can also add the "f-study" figure here.

Table S4: Comparison of the integral value: I_0 for both GMMT and MC at the three sampled temperatures.

I_0						
	T=300K		T=600K		T=900K	
M	MC	GMMT	MC	GMMT	MC	GMMT
100	1.39461E-11	9.55742E-08	3.02496E-09	1.65088E-06	3.31088E-08	2.69035E-05
200	2.06516E-09	3.65672E-07	3.96318E-08	6.27694E-06	4.91988E-07	4.39558E-05
400	1.23783E-08	1.01378E-06	2.3962E-07	1.26578E-05	7.55917E-06	0.000118043
800	6.15616E-08	2.18095E-06	7.7453E-07	1.80321E-05	1.20119E-05	0.000228472
1600	1.48266E-07	6.38479E-06	2.40914E-06	3.18131E-05	2.8871E-05	0.000341311
3200	4.81879E-07	1.04253E-05	4.29241E-06	5.81652E-05	7.15512E-05	0.000327998
6400	1.12956E-06	1.53288E-05	1.29493E-05	6.91736E-05	0.000104845	0.000343917
12800	3.00258E-06	1.78078E-05	2.29981E-05	7.56984E-05	0.000250827	0.000383367
25600	6.33145E-06	2.02208E-05	4.07486E-05	8.2263E-05	0.000310437	0.000406697
51200	9.43088E-06	1.98791E-05	4.83783E-05	8.55447E-05	0.0004321	0.000425287
102400	1.09903E-05	2.09088E-05	6.8707E-05	8.32246E-05	0.000465654	0.00042745
204800	1.39561E-05	2.15654E-05	7.15866E-05	8.5882E-05	0.000453419	0.000454288
409600	1.69523E-05	2.11008E-05	8.26041E-05	8.71467E-05	0.000454069	0.000450418
1000000	1.76751E-05	2.17112E-05	8.5331E-05	8.74332E-05	0.000460528	0.000459008
10000000	2.14009E-05	2.18084E-05	8.78547E-05	8.75992E-05	0.000461327	0.000458956

Table S5: Comparison of the integral value: I_1 for both GMMT and MC at the three sampled temperatures.

I_0						
	T=300K		T=600K		T=900K	
M	MC	GMMT	MC	GMMT	MC	GMMT
100	1.13592E-05	6.95014E-05	0.000101097	0.000711176	0.001529421	0.006003567
200	2.17728E-05	0.000132919	0.000278855	0.000868121	0.002486282	0.00653426

400	6.56515E-05	0.00018488	0.000637409	0.001298525	0.00653253	0.008127894
800	0.000134787	0.000208093	0.000866886	0.001526093	0.007465361	0.009845447
1600	0.000174089	0.00031198	0.001061197	0.001705091	0.008942861	0.010722366
3200	0.000216797	0.000344571	0.001671202	0.001788	0.010113335	0.01038453
6400	0.000252959	0.000400465	0.001666576	0.001850151	0.009955504	0.010903678
12800	0.000328493	0.000431772	0.001746796	0.001929037	0.01075448	0.010864165
25600	0.000377224	0.000427253	0.001981576	0.001974446	0.010795417	0.011261555
51200	0.000394855	0.000431026	0.001940212	0.001990061	0.011114366	0.011190199
102400	0.00040682	0.000431939	0.001926065	0.002008729	0.011306007	0.01126997
204800	0.000422028	0.000433274	0.001964185	0.001983102	0.011212416	0.011217375
409600	0.000419485	0.000435059	0.001974986	0.001996672	0.011166129	0.011268843
1000000	0.000434981	0.000433495	0.001985937	0.001992751	0.01122881	0.011231525
10000000	0.000434505	0.000436297	0.001993728	0.001993238	0.011230763	0.011230453

Table S6: Comparison of the integral value: I_0 for both GMMT and MC at the three sampled temperatures.

I_0						
	T=300K		T=600K		T=900K	
M	MC	GMMT	MC	GMMT	MC	GMMT
100	0.000448294	0.000887913	0.002881924	0.006498295	0.030141317	0.042088995
200	0.000809482	0.001674522	0.005477109	0.007993142	0.040063903	0.059626546
400	0.001344182	0.002029953	0.008299585	0.009997109	0.050249982	0.061237744
800	0.001756535	0.002533781	0.009194785	0.010513619	0.056305494	0.05938331
1600	0.002140908	0.002361598	0.011225191	0.011397438	0.06009715	0.062138586
3200	0.00218255	0.002612585	0.011716093	0.011735305	0.059556469	0.061652826
6400	0.002458438	0.002631951	0.011278861	0.011958729	0.061494533	0.062280312
12800	0.002590239	0.002698756	0.01197198	0.011902882	0.063908975	0.062031493

25600	0.002716953	0.002689961	0.011820705	0.011788868	0.062952725	0.062248452
51200	0.002665248	0.002722938	0.012003694	0.012069246	0.062199121	0.061893694
102400	0.002719589	0.002714493	0.01218336	0.012070302	0.061871327	0.062317827
204800	0.00274874	0.00275786	0.012115489	0.012063351	0.062320991	0.062426984
409600	0.002754343	0.002744849	0.01209348	0.012056579	0.062366743	0.062174981
1000000	0.002742576	0.002741934	0.012067404	0.012073592	0.062264586	0.062379202
10000000	0.002742466	0.002745126	0.012077618	0.01207951	0.062322769	0.062339308

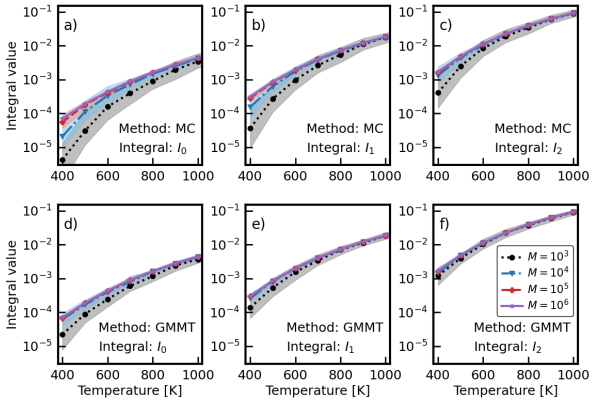

Figure S1: Demonstration of variability of MC (first row) and GMMT (second row) integration results as a function of temperature, for increasing number of integration samples, M. The quantities I_0, I_1, and I_2 are shown in the first, second and third columns, respectively. The line plots depict the medians, and the corresponding color cloud indicates 25% and 75% quantiles among 50 identical integrations.

In order to reduce the variability of a single integration, we reported the median values out of 50 replica simulations for both MC and GMMT cases. This variability is presented in Figure S1. The figure illustrates median as well as first and third quartiles of integration results out of 50 replica integrations, for all considered temperature values and for an increasing number of integration samples for each case.

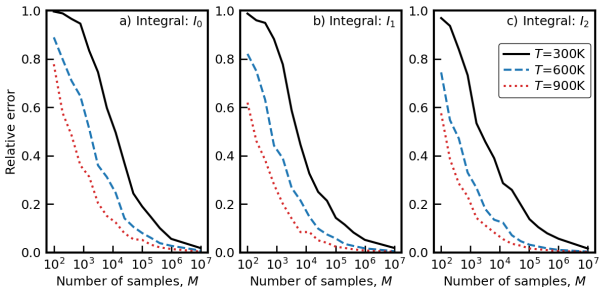

Figure S2: Convergence of GMMT estimate of each integral as the number of integration samples M increases.

Thermodynamic properties

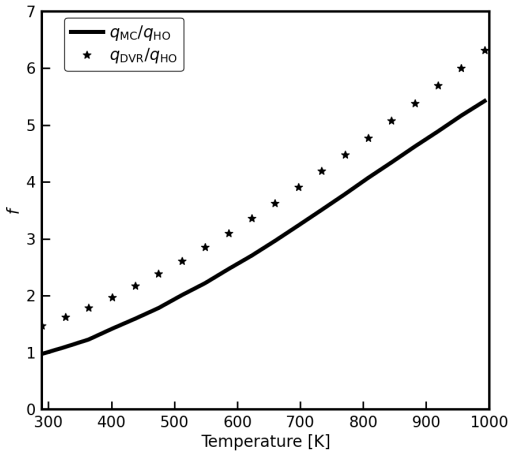

Figure S3: The anharmonic correction factor evaluated with PSI and direct state counting for CH_3/Ni(111).

The anharmonic correction factor f is plotted in Fig. S3 for the DVR and PSI methods, showing that it increases with temperature and ranges from approximately 1.5 to 6.5 at 300-1000 K, with excellent agreement over the entire temperature range.