

# An investigation of free-energy-averaged (coarse-grained) potentials for fluid adsorption on heterogeneous solid surfaces

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## Supplementary Information

The following Chebyshev polynomial form is used to fit the discrete free-energy-averaged (FEA) fluid–solid potential

$$\beta\mathcal{W}^{\text{fit}}(D) = \sum_{i=0}^n c_i T_i(D') \quad (1)$$

where  $n + 1$  is the number of coefficients used in the polynomial.  $c_i$  is the  $i^{\text{th}}$  Chebyshev coefficient and  $D'$  is the scaled version, always in the range  $[-1, 1]$ , of the distance  $D$

$$D' = \frac{D - 0.5(D_{\text{max}} + D_{\text{min}})}{0.5(D_{\text{max}} - D_{\text{min}})} \quad (2)$$

$T_i$  is the  $i^{\text{th}}$  Chebyshev polynomial term given by following recurrence relation

$$\begin{aligned} T_0 &= 1 \\ T_1(x) &= x \\ T_{i+2}(x) &= 2xT_{i+1}(x) - T_i(x) \end{aligned} \quad (3)$$

$D_{\text{min}}$  and  $D_{\text{max}}$  are the minimum and maximum limits considered for fluid–solid distance in the free-energy-averaged (FEA) potential. The coefficients  $c_i$  are obtained using orthogonality condition of Chebyshev polynomials and are provided in the following tables.

Table 1: Chebyshev polynomial coefficients to approximate FEA potential of methane interacting with graphite containing homogeneous graphene surface layer

$c_1 - c_{26}$	$c_{27} - c_{52}$	$c_{53} - c_{78}$	$c_{79} - c_{104}$	$c_{105} - c_{130}$	$c_{131} - c_{151}$
-0.508259	0.000202	0.000092	-0.000129	0.000171	-0.000005
0.378714	-0.000204	-0.000094	0.000068	-0.000201	-0.000039
0.802759	0.000099	0.000107	-0.000008	0.000198	0.000067
-1.574446	0.000067	-0.000107	-0.000038	-0.000160	-0.000076
1.766786	-0.000107	0.000079	0.000072	0.000083	0.000071
-1.571205	0.000155	-0.000049	-0.000093	0.000011	-0.000053
1.219075	-0.000267	0.000018	0.000097	-0.000106	0.000029
-0.856367	0.000231	0.000041	-0.000089	0.000181	-0.000004
0.553093	-0.000063	-0.000113	0.000081	-0.000221	-0.000018
-0.332628	-0.000014	0.000158	-0.000070	0.000214	0.000037
0.187118	0.000039	-0.000181	0.000059	-0.000164	-0.000045
-0.096404	-0.000109	0.000176	-0.000053	0.000082	0.000044
0.043450	0.000131	-0.000128	0.000048	0.000015	-0.000033
-0.015510	-0.000077	0.000042	-0.000033	-0.000111	0.000015
0.001819	0.000069	0.000046	0.000011	0.000180	0.000009
0.004190	-0.000062	-0.000127	0.000014	-0.000210	-0.000031
-0.005461	-0.000026	0.000188	-0.000046	0.000199	0.000049
0.004554	0.000110	-0.000212	0.000085	-0.000148	-0.000059
-0.003571	-0.000110	0.000187	-0.000114	0.000069	0.000058
0.002589	0.000102	-0.000130	0.000138	0.000014	-0.000047
-0.001445	-0.000093	0.000051	-0.000148	-0.000087	0.000027
0.000623	0.000040	0.000039	0.000135	0.000136	
-0.000181	0.000008	-0.000121	-0.000093	-0.000153	
-0.000287	-0.000008	0.000171	0.000033	0.000141	
0.000535	0.000023	-0.000187	0.000038	-0.000105	
-0.000370	-0.000067	0.000172	-0.000112	0.000057	

Table 2: Chebyshev polynomial coefficients to approximate FEA potential of methane interacting with graphite that contains chemical heterogeneities in the surface graphene layer

$c_1 - c_{26}$	$c_{27} - c_{52}$	$c_{53} - c_{78}$	$c_{79} - c_{104}$	$c_{105} - c_{130}$	$c_{131} - c_{151}$
-1.070652	0.006332	-0.000204	-0.000115	0.000191	-0.000138
1.398279	-0.004102	0.000238	0.000041	-0.000160	0.000137
0.224479	0.001846	-0.000167	0.000028	0.000101	-0.000113
-1.600873	0.000215	0.000180	-0.000076	-0.000027	0.000071
2.164310	-0.001839	-0.000128	0.000146	-0.000037	-0.000015
-2.054791	0.002090	0.000023	-0.000186	0.000090	-0.000040
1.610753	-0.001605	-0.000070	0.000170	-0.000136	0.000088
-1.086480	0.001031	0.000097	-0.000160	0.000166	-0.000130
0.649661	0.000021	0.000026	0.000142	-0.000177	0.000159
-0.367744	-0.000903	-0.000080	-0.000073	0.000175	-0.000171
0.217179	0.000872	0.000082	-0.000009	-0.000156	0.000173
-0.153616	-0.000659	-0.000183	0.000085	0.000123	-0.000160
0.137930	0.000526	0.000242	-0.000172	-0.000088	0.000127
-0.130507	0.000008	-0.000207	0.000239	0.000052	-0.000085
0.110932	-0.000506	0.000211	-0.000264	-0.000007	0.000050
-0.081859	0.000576	-0.000204	0.000269	-0.000039	-0.000025
0.048201	-0.000613	0.000156	-0.000241	0.000078	0.000010
-0.014973	0.000548	-0.000182	0.000167	-0.000111	0.000000
-0.009218	-0.000235	0.000201	-0.000088	0.000126	-0.000009
0.021486	0.000110	-0.000108	0.000026	-0.000114	0.000013
-0.024431	-0.000115	0.000032	0.000038	0.000085	-0.000009
0.019550	-0.000086	-0.000005	-0.000095	-0.000046	
-0.010521	0.000149	-0.000071	0.000132	-0.000001	
0.002732	0.000048	0.000135	-0.000164	0.000042	
0.002729	-0.000093	-0.000130	0.000193	-0.000076	
-0.006189	0.000073	0.000128	-0.000202	0.000112	

Table 3: Chebyshev polynomial coefficients to approximate FEA potential of methane interacting with graphite that contains geometric heterogeneities (vacancies) in the surface graphene layer

$c_1 - c_{26}$	$c_{27} - c_{52}$	$c_{53} - c_{78}$	$c_{79} - c_{104}$	$c_{105} - c_{130}$	$c_{131} - c_{151}$
0.677863	-0.000564	0.010054	0.005812	0.001174	0.000084
-1.631478	-0.037636	-0.001700	-0.001328	-0.000723	-0.000163
2.002336	0.034727	-0.007564	-0.003775	-0.000388	0.000157
-1.775072	-0.002578	0.009157	0.005302	0.001249	-0.000045
0.991006	-0.025136	-0.001649	-0.002334	-0.001258	-0.000081
-0.319527	0.025623	-0.008020	-0.002291	0.000506	0.000101
0.240559	-0.003728	0.011205	0.004629	0.000391	0.000037
-0.627857	-0.016842	-0.005140	-0.002971	-0.000816	-0.000262
0.995743	0.017966	-0.005017	-0.001070	0.000590	0.000417
-0.978421	-0.002574	0.010590	0.004165	-0.000023	-0.000376
0.604880	-0.012142	-0.006891	-0.003984	-0.000377	0.000145
-0.188305	0.012733	-0.002671	0.000988	0.000293	0.000134
0.002222	-0.001048	0.009827	0.002176	0.000180	-0.000273
-0.072628	-0.009750	-0.008678	-0.003079	-0.000660	0.000161
0.219678	0.009500	0.000532	0.001398	0.000803	0.000139
-0.250606	-0.000175	0.007499	0.001153	-0.000524	-0.000430
0.125159	-0.007828	-0.008818	-0.002420	0.000013	0.000519
0.042260	0.006291	0.002827	0.001550	0.000406	-0.000355
-0.117349	0.002894	0.005067	0.000506	-0.000497	0.000063
0.065538	-0.009805	-0.008219	-0.001969	0.000260	0.000153
0.039738	0.007029	0.004262	0.001700	0.000097	-0.000160
-0.097534	0.002981	0.003079	-0.000041	-0.000341	
0.067514	-0.010879	-0.007544	-0.001574	0.000365	
0.008809	0.009281	0.005760	0.001918	-0.000228	
-0.060027	0.000512	0.000359	-0.000917	0.000075	
0.049965	-0.009655	-0.005587	-0.000483	-0.000024	

Table 4: Chebyshev polynomial coefficients to approximate FEA potential of methane interacting with graphite that contains both chemical and geometric heterogeneities in the surface graphene layer

$c_1 - c_{26}$	$c_{27} - c_{52}$	$c_{53} - c_{78}$	$c_{79} - c_{104}$	$c_{105} - c_{130}$	$c_{131} - c_{151}$
0.297739	0.003845	0.009629	0.005631	0.000392	0.000049
-1.022739	-0.035819	-0.004602	-0.003553	-0.000678	0.000161
1.679324	0.030644	-0.004505	-0.001360	0.000267	-0.000172
-1.596716	-0.001044	0.009571	0.004997	0.000434	0.000004
0.765137	-0.023706	-0.006122	-0.004551	-0.000852	0.000176
-0.004476	0.024538	-0.002569	0.000697	0.000712	-0.000195
-0.083643	-0.005207	0.008860	0.003222	-0.000175	0.000017
-0.370721	-0.014308	-0.007458	-0.004191	-0.000366	0.000213
0.815421	0.017712	-0.000362	0.001797	0.000607	-0.000287
-0.840265	-0.005930	0.007747	0.001777	-0.000481	0.000104
0.484049	-0.007539	-0.008240	-0.003636	0.000125	0.000251
-0.092021	0.010429	0.001581	0.002548	0.000227	-0.000550
-0.055454	-0.002033	0.006372	0.000213	-0.000391	0.000591
-0.047147	-0.007683	-0.008868	-0.002244	0.000311	-0.000347
0.203693	0.009095	0.003909	0.002049	-0.000035	-0.000020
-0.227262	-0.001736	0.004130	-0.000050	-0.000304	0.000284
0.097027	-0.006776	-0.008476	-0.001967	0.000517	-0.000290
0.060882	0.008109	0.005755	0.002408	-0.000459	0.000060
-0.119766	-0.001110	0.001565	-0.001072	0.000131	0.000223
0.060589	-0.006878	-0.007409	-0.000922	0.000297	-0.000362
0.038153	0.007825	0.007148	0.002118	-0.000578	0.000268
-0.084632	-0.000915	-0.001466	-0.001836	0.000550	
0.051203	-0.007376	-0.004626	0.000564	-0.000239	
0.016963	0.009298	0.006315	0.000623	-0.000145	
-0.056652	-0.002861	-0.002693	-0.000947	0.000359	
0.041808	-0.006133	-0.002860	0.000393	-0.000295	