Supporting Information

Complete Calculation Array and Reproducibility Protocol for the Finite Single-Cell Model of CO_2 Adsorption on Zeolite NaY NIST RM 8850

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S1. Scope of the Supporting Information

This Supporting Information contains the complete numerical array used to reproduce the finite single-cell calculation for CO_2 adsorption on zeolite NaY NIST RM 8850. For each experimental point, the temperature and pressure determine the affinity variable x. The admissible cell states, finite partition function, state probabilities, cell moments, calculated adsorption, and residual diagnostics are then evaluated.

The calculation uses the structural quantities and fitted parameter set reported in the main article throughout the Supporting Information. The numerical pathway is specified from the experimental quantities to the affinity variable, state weights, state probabilities, cell moments, calculated adsorption, and residual diagnostics.

S2. Input quantities and notation

Each experimental point is specified by the temperature T, pressure p, experimental absolute adsorption q_exp, and expanded uncertainty U. The expanded uncertainty is treated as corresponding to coverage factor k = 2. The standard uncertainty is therefore

$$u = U/2.$$

The residual and uncertainty-normalized residual are defined as

$$\Delta q = q_{calc} - q_{exp}, \quad z = \Delta q/u.$$

The mean relative error reported in Section S9 is defined as $N^{-1}\Sigma|\Delta q_i|/q_{exp,i} \times 100\%$.

The symbols used below are: v_c, cell volume; β, effective excluded configurational volume per molecule; ω, integer cell capacity; ν_{mi}, micropore volume per unit mass; C_{mmol}, conversion factor from mean cell loading to mmol g^{-1}; i, number of CO_2 molecules in the cell; P_i, probability of state i; $n = \langle i \rangle$, mean cell loading; Var(i), variance of cell loading; K(T), temperature-dependent affinity coefficient; and x, dimensionless affinity variable.

S3. Fixed quantities and model parameters

The pressure-based calculation uses

$$x = K(T)p,$$

with p expressed in MPa. The fixed structural quantities for NaY NIST RM 8850 are $v_c = 958.2$ Å^3, ω = 14, and $\nu_{mi} = 0.358$ cm^3 g^{-1}. The corresponding conversion factor is $C_{mmol} = 0.6204059549658079$ mmol g^{-1} per unit mean cell loading, and the structural limiting adsorption is $q_{max} = C_{mmol} \times 14 = 8.686$ mmol g^{-1}.

The fitted parameters for CO_2 are $K_0 = 0.0013229$ MPa^{-1}, $E_{ads} = 33.675$ kJ mol^{-1}, and β = 57.542 Å^3. The temperature dependence of the affinity coefficient is

$$K(T) = K_0 \exp(E_{ads}/(RT)),$$

with $R = 0.008314462618$ kJ mol^{-1} K^{-1}.

Table S1. Affinity coefficients used in the calculation.

T, K	K(T), MPa⁻¹
298.06	1054.176116
333.06	252.789540
353.05	126.978770
393.00	39.561288

S4. Calculation procedure for one experimental point

For a point specified by T and p, the affinity coefficient K(T) is calculated from the expression in Section S3, and the dimensionless affinity variable is x = K(T)p.

The cell occupancy is enumerated as i = 0, 1, ..., 14. The free volume of state i is

$$V_{free}(i) = v_c - i\beta.$$

Only states satisfying $V_{free}(i) > 0$ are included in the statistical sum. For an admissible state, the state weight is

$$w_i = (x^i/i!)\,(1 - i\beta/v_c)^i,$$

with $w_0 = 1$. For numerical stability, weights are evaluated in logarithmic form:

$$\ln w_i = i \ln x - \ln(i!) + i \ln(1 - i\beta/v_c).$$

The maximum logarithmic weight $L_{max} = \max \ln w_i$ is subtracted before exponentiation. The reduced weights are $w_i^* = \exp(\ln w_i - L_{max})$, and the normalized probability of state i is

$$P_i = w_i^*/\Sigma w_i^*,$$

where the sum is taken over admissible states.

The mean cell loading, second moment, loading variance, calculated adsorption, residual, and normalized residual are calculated as

$$n = \langle i \rangle = \Sigma\, iP_i,\ M_2 = \Sigma\, i^2P_i,\ \mathrm{Var}(i) = M_2 - n^2,$$

$$q_{calc} = C_{mmol}\, n,\ \Delta q = q_{calc} - q_{exp},\ z = \Delta q/u,$$

with all sums taken over admissible states.

S5. Worked numerical example

A numerical check is given for T = 298.06 K, p = 1.505 MPa, q_{exp} = 7.823 mmol g⁻¹, and U = 0.022 mmol g⁻¹. At this temperature, K(T) = 1054.176116 MPa⁻¹, so x = 1054.176116 × 1.505 = 1586.535.

For the highest occupancy state, $V_{free}(14) = 958.2 - 14 \times 57.542 = 152.612$ Å³. This value is positive, so all states from i = 0 to i = 14 are admissible for this calculation.

Table S2. Dominant state contributions for the control point T = 298.06 K and p = 1.505 MPa.

i	$V_{free}(i)$, Å³	ln w_i	w_i^*	P_i
10	382.780	49.413	0.016370	0.007656
11	325.238	51.675	0.157167	0.073504
12	267.696	53.142	0.681809	0.318870
13	210.154	53.525	1.000000	0.467683
14	152.612	52.259	0.281915	0.131847

The complete probability distribution gives n = ⟨i⟩ = 12.641224 and Var(i) = 0.692095. The calculated adsorption is q_{calc} = 0.6204059549658079 × 12.641224 = 7.842691 mmol g⁻¹. Therefore Δq = 7.842691 - 7.823 = +0.019691 mmol g⁻¹. Since u = U/2 = 0.0110 mmol g⁻¹, the normalized residual is z = +1.790.

S6. Complete calculation array

Table S3 reports the full numerical array. Values are rounded for tabulation; all summary metrics are calculated before rounding.

Table S3. Complete calculation array for CO_2 adsorption on zeolite NaY NIST RM 8850, part 1 of 2.

T, K	p, MPa	q_exp	U	u	K(T)	x	n	Var(i)	q_calc	Δq	z
298.06	3.008	8.160	0.022	0.0110	1054.176	3170.962	13.071	0.551	8.109	-0.051	-4.633
298.06	2.509	8.070	0.022	0.0110	1054.176	2644.928	12.967	0.586	8.045	-0.025	-2.267
298.06	2.010	7.961	0.022	0.0110	1054.176	2118.894	12.833	0.631	7.961	+0.000	+0.033
298.06	1.505	7.823	0.022	0.0110	1054.176	1586.535	12.641	0.692	7.843	+0.020	+1.790
298.06	1.005	7.615	0.022	0.0110	1054.176	1059.447	12.343	0.786	7.658	+0.043	+3.884
298.06	0.750	7.459	0.022	0.0110	1054.176	790.632	12.102	0.863	7.508	+0.049	+4.462
298.06	0.504	7.234	0.022	0.0110	1054.176	531.305	11.736	0.980	7.281	+0.047	+4.281
298.06	0.254	6.801	0.022	0.0110	1054.176	267.761	10.984	1.224	6.815	+0.014	+1.229
298.06	0.110	6.133	0.021	0.0105	1054.176	115.959	9.808	1.600	6.085	-0.048	-4.577
298.06	0.074	5.740	0.021	0.0105	1054.176	78.009	9.134	1.803	5.667	-0.073	-6.981
298.06	0.053	5.355	0.021	0.0105	1054.176	55.871	8.503	1.976	5.275	-0.080	-7.576
298.06	0.033	4.710	0.020	0.0100	1054.176	34.788	7.512	2.204	4.660	-0.050	-4.971
333.06	2.908	7.492	0.022	0.0110	252.790	735.112	12.038	0.883	7.469	-0.023	-2.124
333.06	2.499	7.399	0.022	0.0110	252.790	631.721	11.901	0.927	7.384	-0.015	-1.408
333.06	2.005	7.260	0.022	0.0110	252.790	506.843	11.689	0.995	7.252	-0.008	-0.708
333.06	1.502	7.065	0.022	0.0110	252.790	379.690	11.388	1.093	7.065	+0.000	+0.023
333.06	1.003	6.775	0.021	0.0105	252.790	253.548	10.917	1.246	6.773	-0.002	-0.217
333.06	0.750	6.545	0.021	0.0105	252.790	189.592	10.537	1.369	6.537	-0.008	-0.753
333.06	0.504	6.193	0.021	0.0105	252.790	127.406	9.956	1.554	6.177	-0.016	-1.519
333.06	0.253	5.451	0.021	0.0105	252.790	63.956	8.766	1.906	5.438	-0.013	-1.220
333.06	0.111	4.304	0.020	0.0100	252.790	28.060	7.029	2.290	4.361	+0.057	+5.655
333.06	0.083	3.851	0.019	0.0095	252.790	20.982	6.349	2.376	3.939	+0.088	+9.288
333.06	0.053	3.193	0.019	0.0095	252.790	13.398	5.270	2.416	3.269	+0.076	+8.042
333.06	0.033	2.548	0.019	0.0095	252.790	8.342	4.145	2.304	2.572	+0.024	+2.480

Table S3. Complete calculation array for CO_2 adsorption on zeolite NaY NIST RM 8850, part 2 of 2.

T, K	p, MPa	q_exp	U	u	K(T)	x	n	Var(i)	q_calc	Δq	z
353.05	2.972	7.068	0.021	0.0105	126.979	377.381	11.381	1.095	7.061	-0.007	-0.656
353.05	2.510	6.945	0.021	0.0105	126.979	318.717	11.191	1.157	6.943	-0.002	-0.177
353.05	2.010	6.778	0.021	0.0105	126.979	255.227	10.925	1.243	6.778	-0.000	-0.017
353.05	1.501	6.543	0.021	0.0105	126.979	190.595	10.544	1.367	6.542	-0.001	-0.136
353.05	1.007	6.184	0.021	0.0105	126.979	127.868	9.962	1.552	6.181	-0.003	-0.330
353.05	0.752	5.892	0.021	0.0105	126.979	95.488	9.488	1.698	5.886	-0.006	-0.550
353.05	0.504	5.439	0.021	0.0105	126.979	63.997	8.767	1.906	5.439	-0.000	-0.004
353.05	0.255	4.517	0.020	0.0100	126.979	32.380	7.353	2.234	4.562	+0.045	+4.454
353.05	0.107	3.194	0.019	0.0095	126.979	13.587	5.304	2.417	3.290	+0.096	+10.146
353.05	0.078	2.756	0.019	0.0095	126.979	9.904	4.546	2.364	2.820	+0.064	+6.771
353.05	0.052	2.229	0.018	0.0090	126.979	6.603	3.619	2.188	2.245	+0.016	+1.811
353.05	0.027	1.626	0.018	0.0090	126.979	3.428	2.332	1.710	1.447	-0.179	-19.915
393.00	3.018	6.111	0.021	0.0105	39.561	119.396	9.855	1.586	6.114	+0.003	+0.267
393.00	2.501	5.926	0.021	0.0105	39.561	98.943	9.548	1.680	5.923	-0.003	-0.241
393.00	2.002	5.693	0.021	0.0105	39.561	79.202	9.161	1.795	5.684	-0.009	-0.893
393.00	1.502	5.362	0.020	0.0100	39.561	59.421	8.624	1.944	5.350	-0.012	-1.165
393.00	0.997	4.843	0.020	0.0100	39.561	39.443	7.785	2.147	4.830	-0.013	-1.319
393.00	0.752	4.445	0.020	0.0100	39.561	29.750	7.162	2.268	4.443	-0.002	-0.175
393.00	0.503	3.840	0.019	0.0095	39.561	19.899	6.223	2.387	3.861	+0.021	+2.209
393.00	0.258	2.819	0.019	0.0095	39.561	10.207	4.617	2.372	2.865	+0.046	+4.792
393.00	0.105	1.711	0.018	0.0090	39.561	4.154	2.675	1.867	1.660	-0.051	-5.684
393.00	0.079	1.417	0.018	0.0090	39.561	3.125	2.177	1.632	1.351	-0.066	-7.357
393.00	0.052	1.064	0.017	0.0085	39.561	2.057	1.569	1.280	0.973	-0.091	-10.679
393.00	0.029	0.759	0.017	0.0085	39.561	1.147	0.953	0.844	0.591	-0.168	-19.715

S7. State probabilities for selected points at 298.06 K

Table S4 reports selected state probability distributions along the 298.06 K isotherm. All probabilities are obtained from the same finite statistical sum as q_calc.

Table S4. State probabilities for selected points at T = 298.06 K.

p, MPa	x	P0	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	n	Var(i)	q_calc
0.033	34.788	0.000001	0.000030	0.000428	0.003531	0.018570	0.065037	0.154015	0.245565	0.258024	0.171568	0.067603	0.014232	0.001354	0.000044	0.000000	7.512	2.204	4.660
0.254	267.761	0.000000	0.000000	0.000000	0.000000	0.000000	0.000008	0.000144	0.001763	0.014262	0.072993	0.221376	0.358716	0.262633	0.065011	0.003093	10.984	1.224	6.815
0.504	531.305	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000004	0.000088	0.001413	0.014349	0.086350	0.277639	0.403344	0.198110	0.018703	11.736	0.980	7.281
1.505	1586.535	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000014	0.000426	0.007656	0.073504	0.318870	0.467683	0.131847	12.641	0.692	7.843
3.008	3170.962	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000029	0.001054	0.020218	0.175295	0.513865	0.289539	13.071	0.551	8.109

Increasing pressure shifts the probability mass toward higher occupancies. The approach to saturation is represented by redistribution of probabilities over the finite set of cell states.

S8. Internal consistency checks

The numerical array satisfies four internal consistency conditions: (1) $\Sigma P_i = 1$ within rounding error; (2) $0 \le n \le 14$; (3) $q_{calc} \le q_{max}$ for all data points; and (4) $V_{free}(i) > 0$ for all admissible states.

The response identity provides a differential consistency check. For the finite single-cell statistical sum,

$$dn/d \ln x = \mathrm{Var}(i).$$

At fixed temperature in the pressure-based regime $x = K(T)p$, this is equivalently $dn/d \ln p = \mathrm{Var}(i)$, and for adsorption $dq_{calc}/d \ln p = C_{mmol}\,\mathrm{Var}(i)$.

For the control point $T = 298.06$ K and $p = 1.505$ MPa, the moment calculation gives $\mathrm{Var}(i) = 0.692094756$. A central finite difference in $\ln x$ with step 0.001 gives $dn/d \ln x = 0.692094759$. The agreement confirms the consistency of the state weights, normalization, probabilities, and cell-loading moments.

S9. Summary metrics and low-pressure residuals

For the full 48-point array, the mean absolute error is 0.0361 mmol g^{-1}, the root-mean-square error is 0.0539 mmol g^{-1}, max $|\Delta q|$ is 0.1792 mmol g^{-1}, the mean relative error is 1.5765 %, mean(z^2) is 33.9036, and max $|z|$ is 19.9149.

For the pressure range $p \ge 0.25$ MPa, the mean absolute error is 0.0158 mmol g^{-1}, the root-mean-square error is 0.0228 mmol g^{-1}, max $|\Delta q|$ is 0.0510 mmol g^{-1}, the mean relative error is 0.2741 %, mean(z^2) is 4.6461, and max $|z|$ is 4.7920.

The largest normalized residuals occur in the low-pressure region. The internal consistency checks confirm that the numerical array remains normalized and satisfies the loading bounds in this region. The low-pressure residuals define the applicability boundary of the statistically equivalent single-cell approximation. In the initial loading region, local differences between adsorption environments in NaY can be more visible than in the main part of the isotherm. Description of this region would require an extension to a heterogeneous cell ensemble or an affinity-parameter distribution; such an extension is not included in the present calculation array.

The complete array documents the calculated adsorption values, internal cell-state distributions, and response quantity Var(i) for every experimental point.