Finite Single-Cell Statistical Model of Equilibrium CO_2 Adsorption on Zeolite NaY NIST RM 8850

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Abstract

Equilibrium adsorption of carbon dioxide on zeolite NaY NIST RM 8850 is analyzed using a finite single-cell statistical model. The reference dataset contains 48 published adsorption points at $T = 298.06, 333.06, 353.05$, and $393.00\,\mathrm{K}$ and $p = 0.027\text{-}3.018\,\mathrm{MPa}$, with reported expanded uncertainties. The micropore space is represented as an ensemble of statistically equivalent independent cells of finite capacity. The cell state is specified by the discrete number of adsorbed particles $i = 0, 1, \ldots, \omega$. The configurational constraint is introduced through the free volume $V_{\text{free}}(i) = v_c - i\beta$. From the finite partition function, monotonicity, the Henry limit, saturation, non-increase of mean loading with β, and the response identity $dn/d(\ln x) = \mathrm{Var}(i) \geq 0$ follow directly. The Langmuir isotherm is obtained as an exact special case at $\omega = 1$ and $\beta = 0$. For CO_2 adsorption on NaY NIST RM 8850, the fitted parameters are $K_0 = (1.3229 \pm 0.114) \times 10^{-3}\,\mathrm{MPa}^{-1}$, $E_{\text{ads}} = 33.675 \pm 0.26\,\mathrm{kJ\ mol}^{-1}$, and $\beta = 57.542 \pm 0.15\,\text{Å}^3$. On the full dataset, MAE = $0.0361\,\mathrm{mmol\ g}^{-1}$ and RMSE = $0.0539\,\mathrm{mmol\ g}^{-1}$. The residuals at $p < 0.15\,\mathrm{MPa}$ mark the low-pressure applicability boundary of the statistically equivalent single-cell approximation.

Keywords: equilibrium adsorption; carbon dioxide; zeolite NaY; NIST RM 8850; single-cell model; finite partition function; uncertainty diagnostics

1. Introduction

Equilibrium adsorption in microporous materials is commonly described by isotherms $q(p, T)$. Standard forms such as the Langmuir, Freundlich, and Dubinin equations, together with their modifications, are useful for fitting experimental data. However, in many cases they are introduced as empirical functional forms rather than derived from a single finite statistical ensemble. As a result, limiting capacity, initial slope, curvature, and response derivatives may be controlled by separate model assumptions.

A finite statistical ensemble is constructed in which probabilities, mean loading, limiting behavior, and response follow from a single finite partition function. The adsorption amount, local-state populations, and pressure sensitivity are obtained within the same statistical framework.

The discrete statistical description of pore filling in zeolites traces back to Ruthven [1] and is discussed in standard adsorption texts [2,3]. Wedler et al. used a cell-based framework for CO_2/CH_4 adsorption on zeolite NaY, including the NIST RM 8850 material [4]. A closed single-cell formulation is obtained in which the admissible states, probabilities, limiting behavior, response identity, structural adsorption scale, and residual diagnostics belong to one finite statistical framework.

NIST RM 8850 provides the reference adsorption system. The published unary CO_2/NaY data define the adsorption scale, and the reported expanded uncertainties define the scale for residual diagnostics. The same dataset supports parameter estimation and identifies the applicability boundary of the statistically equivalent single-cell approximation.

The work has four specific contributions.

1. Axioms A1–A8 define a single-cell equilibrium model of a micropore with a finite number of admissible states.
2. The finite partition function yields monotonicity, the Henry limit, saturation, the adsorption upper bound, and the response identity.
3. A linear free-volume closure suppresses high-loading states configurationally while keeping the energy levels occupancy-independent.
4. Unweighted shape fitting evaluates the isotherm form, and normalized residuals evaluate consistency with the published uncertainty scale.

Table 1. Chemical sample and reference material.

Sample	Information item	Value	Source or model role
Carbon dioxide	Formula	CO_2	Adsorbate in the CO_2/NaY equilibrium adsorption system.
Carbon dioxide	CAS Registry number	124-38-9	Chemical identifier.
Carbon dioxide	Source	BOC	Reported for the source adsorption measurements in Ref. [4].
Carbon dioxide	Initial purity	Mole fraction y = 0.99995	Reported in Ref. [4].
Carbon dioxide	Purification	Not applied	Source purity was taken from Ref. [4].
Carbon dioxide	Final purity	Mole fraction y = 0.99995	Taken from Ref. [4].
Carbon dioxide	Analysis method	Supplier-stated purity	Reported in Ref. [4].
Carbon dioxide	Model role	Pressure input p; model variable x = K(T)p	Thermodynamic input.
Zeolite NaY	Formula or identifier	NIST RM 8850; sodium form of zeolite Y; FAU-type zeolite	Microporous adsorbent.
Zeolite NaY	CAS Registry number or material identifier	1318-02-1; NIST RM 8850	Chemical and reference-material identifiers reported in Refs. [4,5].
Zeolite NaY	Source	NIST Reference Material 8850	Material source reported in Refs. [4,5].
Zeolite NaY	Material status	NIST reference material	Composition and characterization are reported in Refs. [4,5].
Zeolite NaY	Pretreatment	As reported in Ref. [4]	Source material preparation is described in Ref. [4].
Zeolite NaY	Final material status	NIST reference material	Mole-fraction purity is not applicable to the solid reference material.
Zeolite NaY	Analysis method	NIST material characterization	Material data are taken from Refs. [4,5].
Zeolite NaY	Model role	Fixed structural quantities ν_c, ω, and ν_mi	Determine the number of cells per unit mass, the conversion coefficient, and the limiting adsorption.

2. Axiomatics

This section defines the minimal formulation needed to construct a single-cell partition function and derive the adsorption isotherm without hidden fitting terms.

A1. Cell ensemble. The micropore space is represented as an ensemble of local elements called cells. Each cell has a configurational volume $v_c > 0$. The loading states of the cell are enumerated by the discrete number of particles i. The number of admissible particles is finite.

A2. Cell equivalence. At fixed temperature T and reservoir state, the probability distribution over cell states is the same for all cells in the ensemble.

A3. Cell independence. The cells are statistically independent. The probability of a cell state is determined by the reservoir state and the internal constraints of the cell. The base model neglects inter-cell correlations.

A4. Discrete capacity. The cell state is defined by the number of particles $i \in \{0, 1, \dots, \omega\}$, where ω is the structural capacity of the cell. The parameter ω is an integer structural capacity, not a continuous fitted parameter.

A5. Thermodynamic input. The cell is in equilibrium with the reservoir. The pressure p is expressed in MPa. When gas non-ideality is included, the fugacity $f(p,T) = \varphi(p,T)\,p$ is used in the same units.

A6. Affinity parameter. The distribution over cell states is governed by the dimensionless parameter $x = K(T)\,p$. With fugacity input, $x = K(T)\,f(p,T)$. The function $K(T)$ has units of MPa^{-1}.

A7. Configurational constraint. The free volume of the cell at loading i particles is given by the linear law

$$V_{\text{free}}(i) = v_c - i\beta \tag{1}$$

Here β is the effective excluded configurational volume per particle. The parameter β describes the loss of accessible configurational space as loading increases, while the energy levels remain occupancy-independent.

A8. Admissible states. State i is included in the ensemble only when $V_{\text{free}}(i) > 0$. The actual upper loading bound is

$$i_{max} = min\left(\omega, max\{i : v_c - i\beta > 0\}\right) \tag{2}$$

At $\beta = 0$, $i_{max} = \omega$. At $\beta > 0$, $i_{max} = min\left(\omega, \operatorname{floor}\left((v_c - \varepsilon)/\beta\right)\right)$, $\varepsilon \to 0^+$.

The base approximation is restricted to equilibrium regimes governed by local cell statistics. Regimes with significant inter-cell correlations, hysteresis, or kinetic limitations are outside its scope. Practical signs of departure from this regime include persistent systematic residuals, incompatible initial slopes at different temperatures, and improved fits obtained only by changing structural quantities v_c or ω.

3. Partition Function and Adsorption Equation

3.1. State weights

The statistical weight of the state with i particles is given by

$$w_i(x) = \frac{x^i}{i!}\left(1 - \frac{i\beta}{v_c}\right)^i, i = 0, 1, \dots, i_{max} \tag{3}$$

The factor $x^i/i!$ accounts for the reservoir contribution and particle indistinguishability. The factor $(1 - i\beta/v_c)^i$ implements the free-volume closure generated by $V_{\text{free}}(i) = v_c - i\beta$. As i increases, the accessible configurational space decreases and high-loading states are entropically suppressed. For $i > i_{\max}$, $w_i = 0$.

The linear law $V_{\text{free}}(i) = v_c - i\beta$ is the minimal free-volume closure of the base single-cell model.

3.2. Partition function, probabilities, and mean loading

The single-cell partition function is

$$Z(x) = \sum_{i=0}^{i_{max}} w_i(x) \tag{4}$$

Since $w_0 = 1$ and the number of terms is finite, $Z(x) > 0$ for all $x \geq 0$. The probability of state i is

$$P_i(x)=\frac{w_i(x)}{Z(x)} \tag{5}$$

The mean cell loading is

$$n(x)=\sum_{i=0}^{i_{max}} i\,P_i(x) \tag{6}$$

The isotherm $q(p,T)$ follows from the finite ensemble. The weights $w_i(x)$ of the admissible microstates are computed first, and the probabilities $P_i(x)$ and mean loading $\langle i\rangle$ then follow from the partition function $Z(x)$.

3.3. Conversion to absolute adsorption

The micropore volume v_{mi} and the cell volume v_c determine the number of cells per unit mass:

$$N_c=\frac{v_{\mathrm{mi}}}{v_c\times 10^{-24}} \tag{7}$$

Here v_{mi} is expressed in $\mathrm{cm}^3\,\mathrm{g}^{-1}$ and v_c in $\mathrm{Å}^3$. The conversion coefficient to $\mathrm{mmol\ g}^{-1}$ is

$$C=\frac{1000\,N_c}{N_A} \tag{8}$$

The absolute adsorption, reported on the absolute adsorption scale [6], is

$$q(p,T)=C\,n(x),\, x=K(T)\,p \tag{9}$$

The temperature dependence of the affinity coefficient is written as

$$K(T)=K_0\exp\left(\frac{E_{\mathrm{ads}}}{RT}\right) \tag{10}$$

Here $K_0>0$, $E_{\mathrm{ads}}>0$, and $R=8.314\times 10^{-3}\,\mathrm{kJ\ mol^{-1}\,K^{-1}}$. The parameter E_{ads} is used as a positive affinity-energy parameter. With this convention, $K(T)$ increases as temperature decreases, which corresponds to the usual trend for exothermic adsorption.

4. Model Properties

4.1. Response identity and monotonicity

For $x>0$,

$$n(x)=\frac{d\ln Z}{d\ln x}$$

Introduce the operator $D=d/d(\ln x)=x\,d/dx$. Since $w_i(x)$ is proportional to x^i, $D\,w_i=i\,w_i$. Therefore $DZ=\sum i\,w_i$ and $DZ/Z=\sum i\,P_i=n(x)$. Hence $n(x)=D\ln Z$.

Differentiating n with respect to $\ln x$ gives

$$Dn=\sum i(i-n)P_i=\sum i^2P_i-n^2=\mathrm{Var}(i)$$

Thus

$$\frac{dn}{d(\ln x)}=\mathrm{Var}(i)=\sum_{i=0}^{i_{max}}(i-n)^2P_i(x)\ge 0 \tag{11}$$

The isotherm is monotonically non-decreasing with increasing x. Identity (11) provides an internal computational invariant: the numerical derivative $d\langle i\rangle/d\ln x$ must match the variance of cell loading. Physically, $\mathrm{Var}(i)$ characterizes the sensitivity of the cell to changes in the control variable.

4.2. Monotonicity in β

At fixed x, the mean loading $n(x)$ does not increase with increasing β. The logarithmic derivative of the weight with respect to β is

$$s_i(\beta)=\frac{d\ln w_i}{d\beta}=\frac{-i^2}{v_c-i\beta}$$

On the admissible domain $v_c-i\beta>0$, the quantity s_i is negative and decreases with i. Then

$$\frac{dn}{d\beta}=\frac{1}{2}\sum_i\sum_j(i-j)(s_i-s_j)P_iP_j\le 0$$

The inequality follows from the fact that $(i-j)(s_i-s_j)\le 0$. If increasing β reduces i_{max}, the highest-loading states are removed, which also cannot increase n. Therefore, the mean loading is non-increasing in β over the entire admissible range.

4.3. Henry limit

As $x\to 0$, $w_0=1$, $w_1=x(1-\beta/v_c)$, and contributions for $i\ge 2$ are $O(x^2)$. Therefore

$$n(x)=x\left(1-\frac{\beta}{v_c}\right)+O(x^2)$$

For adsorption,

$$q(p,T)=H(T)p+O(p^2) \tag{12}$$

where $H(T)=C(1-\beta/v_c)K(T)$. The linear regime exists when $v_c>\beta$. The factor $1-\beta/v_c$ reflects the configurational accessibility of the cell to a single molecule within the chosen free-volume closure.

4.4. Saturation

As $x\to\infty$, the state with maximum admissible loading $i=i_{max}$ dominates. Therefore $n(x)\to i_{max}$ and

$$q_{max}=C\,i_{max} \tag{13}$$

The parameters v_c, β, and ω determine the maximum admissible cell loading i_{max}. After conversion with v_{mi}/v_c, this cell-level bound fixes the limiting adsorption.

4.5. Langmuir isotherm as a special case

At $\omega=1$ and $\beta=0$, only states $i=0$ and $i=1$ are admissible. Then $Z=1+x$ and $n=x/(1+x)$. Consequently,

$$q(p,T)=\frac{Cx}{1+x} \tag{14}$$

The Langmuir isotherm is an exact single-occupancy reduction of the finite cell statistics.

5. Parameters and Identification

5.1. Structural and fitted parameters

The structural parameters v_c, ω, and v_{mi} are fixed from material data and determine the number of cells per unit mass, the conversion coefficient C, and the structural adsorption scale.

The fitted parameters are K_0, E_{ads}, and β. In practice, estimation is conveniently carried out in the variables $\ln K_0$, E_{ads}, and β because $K_0 > 0$ and the derivatives with respect to $\ln K_0$ are directly connected to the response identity.

The integer-valued parameter ω is treated as a structural capacity and checked by scanning neighboring structurally admissible values, for example $\omega = 13$, 14, and 15, with full re-estimation of the continuous parameters. Similar metrics for neighboring capacities indicate that the measured range resolves the isotherm shape but leaves the structural capacity ω unresolved. In this case, ω remains fixed on structural grounds.

At low loading, a scale degeneracy arises. As $x \to 0$, $q \approx C\left(1-\beta/v_c\right)K\left(T\right)p$. Here the scale C and the function $K\left(T\right)$ enter only through their product. Stable separation requires either independent structural fixing of C or data approaching saturation.

5.2. Objective function and uncertainty diagnostics

The parameters are estimated by minimizing the unweighted sum of squared deviations

$$S=\sum \Delta q_k^2,\Delta q_k=q_{\mathrm{model},k}-q_{\mathrm{exp},k} \tag{15}$$

The unweighted objective function captures the isotherm shape without imposing predetermined weight redistributions across pressure regions. The reported expanded uncertainties U_i define the residual-diagnostic scale through the standard uncertainties $u_\mathrm{i} = U_\mathrm{i}/k$ [7]:

$$z_k=\frac{\Delta q_k}{u_k},u_k=\frac{U_k}{2} \tag{16}$$

where U_i is the expanded uncertainty at coverage factor k. This separation distinguishes shape reproduction from consistency with the published uncertainty scale.

5.3. Standard errors

Standard errors are estimated through the Jacobian matrix J with elements $J_{kj}=\partial q_k/\partial\theta_j$, where θ is the vector of fitted parameters. Near the minimum, the approximation

$$\mathrm{Cov}\left(\theta\right)=s^2\left(J^T J\right)^{-1},s^2=\frac{S}{N-m} \tag{17}$$

is used. Here N is the number of experimental data points and m is the number of fitted parameters. From identity (11), the following analytical derivative checks follow:

$$\frac{\partial q}{\partial\left(\ln K_0\right)}=C\,\mathrm{Var}\left(i\right),\frac{\partial q}{\partial E_{\mathrm{ads}}}=\frac{C\,\mathrm{Var}\left(i\right)}{RT} \tag{18}$$

6. Verification on NIST RM 8850

6.1. Data and calculation regime

The model was evaluated against 48 published unary CO_2 adsorption points on zeolite NaY NIST RM 8850 at nominal temperature branches of 298.06, 333.06, 353.05, and 393.00 K and pressures of 0.027–3.018 MPa [4]. These nominal branch temperatures were used consistently in the pressure-based calculation and in the Supporting Information calculation array. The values are reported as absolute adsorption with expanded uncertainties at coverage factor $k = 2$.

Table 2. Reference adsorption data used for model evaluation.

Data element	Content	Role in the analysis
Reference source	Published CO_2 adsorption data for zeolite NaY	Basis for fitting and model evaluation.

Data element	Content	Role in the analysis
	NIST RM 8850 [4]	
Number of points	48 equilibrium adsorption points	Full dataset for parameter estimation and quality metrics.
Temperatures	298.06, 333.06, 353.05, and 393.00 K	Test of the temperature dependence of $K(T)$.
Pressure range	0.027-3.018 MPa	Test of the initial region, working adsorption region, and approach to saturation.
Reported uncertainties	Expanded uncertainties U with coverage factor $k=2$	Defines $u_i = U_i/k$ and normalized residuals z_i.
Calculated quantities	q_{model}, Δq, z, MAE, RMSE, $\text{mean}(z^2)$, fitted parameters	Results of the statistical model calculation and uncertainty diagnostics.

The calculation was performed in the pressure-based regime p and $\varphi = 1$. This regime allows direct reproduction from the tabulated values of p, T, q, and U without choosing an equation of state. At 298.06 K and 3.018 MPa, the fugacity coefficient of CO_2 from the Peng-Robinson equation [8] is approximately 0.84. Therefore, the parameters obtained at $\varphi = 1$ are effective parameters of the chosen thermodynamic input.

In the low-pressure region, this correction is negligible. At $p = 0.027$ MPa, $\varphi \approx 0.998$, so replacing pressure by fugacity changes x by less than 0.2%. Gas non-ideality is therefore too small to account for the low-pressure systematics.

6.2. Structural parameters

For NaY, the following structural values were used [4,5]: $v_c = 958.2$ Å^3, $\omega = 14$, and $v_{mi} = 0.358$ cm^3 g^{-1}. From eqs 7 and 8, $C = 0.6204$ mmol g^{-1}. The limiting adsorption predicted by the structural cell capacity is $q_{max} = 8.686$ mmol g^{-1}. The structural quantities v_c, ω, and v_{mi} fix this value.

For the fitted β value, $v_c/\beta = 16.7 > \omega = 14$. Therefore $i_{max} = 14$ and all states $i = 0, \ldots, 14$ are admissible. The free volume at maximum loading is $V_{\text{free}}(14) = 958.2 - 14 \times 57.542 = 152.612\,\text{Å}^3$.

A scan of neighboring capacities shows that $\omega = 13$ worsens the quality metrics, whereas $\omega = 15$ gives metrics close to those at $\omega = 14$. The measured pressure range constrains the isotherm shape but leaves capacities above $\omega = 14$ unresolved. The capacity ω is therefore fixed on structural grounds.

6.3. Estimated parameters

The parameter set used for the reported calculation array and Supporting Information is, for the full dataset $N = 48$ [4], $K_0 = (1.3229 \pm 0.114) \times 10^{-3}\,\text{MPa}^{-1}$, $E_{\text{ads}} = 33.675 \pm 0.26\,\text{kJ mol}^{-1}$, and $\beta = 57.542 \pm 0.15\,\text{Å}^3$.

The parameter correlations are $\text{corr}(K_0, E_{\text{ads}}) = -0.991$, $\text{corr}(K_0, \beta) = -0.273$, and $\text{corr}(E_{\text{ads}}, \beta) = 0.364$. The strong anti-correlation between K_0 and E_{ads} is associated with the exponential temperature dependence and the limited temperature range. The correlations of β with the affinity parameters are moderate, indicating that the configurational contribution is separable from the temperature scale of affinity in this dataset.

Table 3. Structural quantities, fitted parameters, derived quantities, and calculation regime.

Quantity	Value	Unit	Status and role
v_c	958.2	Å^3	Fixed structural cell volume.
ω	14	-	Fixed integer cell capacity.
v_{mi}	0.358	cm^3 g^{-1}	Fixed micropore volume of the material.
C	0.6204	mmol g^{-1}	Derived conversion coefficient from mean cell loading to adsorption.

Quantity	Value	Unit	Status and role
q_{max}	8.686	mmol g^{-1}	Derived limiting adsorption, $q_{max} = C\omega$.
K_0	$(1.3229 \pm 0.114) \times 10^{-3}$	MPa^{-1}	Fitted affinity pre-exponential parameter.
E_{ads}	33.675 ± 0.26	kJ mol^{-1}	Fitted positive affinity-energy parameter.
β	57.542 ± 0.15	Å^3	Fitted excluded configurational volume per particle.
Thermodynamic input	$x = K(T)p$	-	Pressure-based calculation regime.
Objective function	$S = \sum \Delta q_k^2$	$(\text{mmol g}^{-1})^2$	Unweighted sum of squared deviations.
Uncertainty diagnostics	$z_k = \Delta q_k / u_k$	-	Calculated from U_i/k with $k = 2$; used for residual diagnostics.
Number of fitted data points	48	-	Full reference dataset.

6.4. Numerical check points and internal cell quantities

Selected points from the 298.06 K isotherm are presented in Table 4. They are listed only as numerical check points; the fitted parameters and quality metrics are based on all 48 reference points.

Table 4. Selected numerical check points and internal cell quantities for CO_2 adsorption on zeolite NaY NIST RM 8850 at T = 298.06 K.

p/MPa	x	n	$\text{Var}(i)$	q_{exp}/(mmol g⁻¹)	q_{model}/(mmol g⁻¹)	Δq/(mmol g⁻¹)
0.033	34.788	7.512	2.204	4.710	4.660	-0.050
0.254	267.761	10.984	1.224	6.801	6.815	+0.014
0.504	531.305	11.736	0.980	7.234	7.281	+0.047
1.505	1586.535	12.641	0.692	7.823	7.843	+0.020
3.008	3170.962	13.071	0.551	8.160	8.109	-0.051

All internal quantities in Table 4 are obtained from the same finite partition function. The decrease in $\text{Var}(i)$ with increasing pressure is consistent with the response identity $dn/d(\ln x) = \text{Var}(i)$ and with the approach to saturation.

6.5. Quality metrics

Table 5. Comparison of the single-cell model and the Langmuir isotherm for CO_2 adsorption on zeolite NaY NIST RM 8850 using the full reference dataset, N = 48.

Model	Number of fitted parameters	MAE/(mmol g⁻¹)	RMSE/(mmol g⁻¹)	max |Δq|/(mmol g⁻¹)	mean(z²)
Single-cell model	3	0.0361	0.0539	0.179	33.9
Langmuir isotherm	3	0.242	0.288	0.707	815

Both models have three fitted parameters. The single-cell model additionally uses the structural values v_c, ω, and v_{mi}, which are fixed independently. The comparison with the Langmuir isotherm controls the single-occupancy limit and isolates the contribution of multi-occupancy statistics.

Table 6. Quality metrics of the single-cell model for CO_2 adsorption on zeolite NaY NIST RM 8850 in different pressure ranges.

Range	N	MAE/(mmol g⁻¹)	RMSE/(mmol g⁻¹)	mean(z²)	max |z|
Full dataset	48	0.0361	0.0539	33.9	19.9
$p \geq 0.25$ MPa	32	0.0158	0.0228	4.65	4.79
$p < 0.15$ MPa	16	0.0767	0.0876	92.4	19.9

In the main region of the isotherms, $p \geq 0.25$ MPa, the single-cell model reproduces the data with a small absolute error. Over the full dataset, the uncertainty metric deteriorates due to the low-pressure data points.

6.6. Residual structure and applicability boundary

In the range $p > 0.25$ MPa, the residuals show no persistent dependence on pressure or temperature. The value mean $(z^2) = 4.65$ corresponds to agreement at the level of approximately two standard uncertainties.

At $p < 0.15$ MPa, a temperature-dependent residual structure emerges. At 298 K the residuals are predominantly negative, at 333 K positive, at 353 K they change sign within the isotherm, and at 393 K they are negative. The largest normalized deviations are $|z| = 19.9$ at 353.05 K and 0.027 MPa, and $|z| = 19.7$ at 393.00 K and 0.029 MPa.

The absolute deviations at these points are approximately 0.179 and 0.168 mmol g^{-1}, respectively, whereas the corresponding standard uncertainties are 0.0090 and 0.0085 mmol g^{-1}. This structure exceeds random noise on the published uncertainty scale.

7. Discussion

The single-cell model reproduces the published CO_2/NaY NIST RM 8850 isotherms for $p \geq 0.25$ MPa, whereas the low-pressure residuals define its applicability boundary. In the range $p \geq 0.25$ MPa, MAE = $0.0158\,\mathrm{mmol\ g^{-1}}$ and RMSE = $0.0228\,\mathrm{mmol\ g^{-1}}$. The remaining value $\mathrm{mean}\left(z^2\right) = 4.65$ shows that residuals are larger than the reported standard uncertainties, but they are far smaller than for the Langmuir isotherm on the same dataset. Multi-occupancy cell statistics therefore captures the isotherm shape substantially better than the single-occupancy saturable scheme.

The low-pressure region behaves differently. A single parameter set with fixed ω and β fails to reproduce the initial adsorption behavior at all temperatures. Gas non-ideality is too small to account for this effect. At $p = 0.027$–0.029 MPa, replacing pressure by fugacity changes x by less than 0.2%, while normalized residuals reach $|z| \approx 20$.

The residual pattern is consistent with heterogeneity of local adsorption environments in NaY. CO_2 can interact with non-equivalent sites, including high-affinity cation-associated sites and lower-affinity regions inside the supercage. The single-cell model averages over these environments with one affinity scale. This averaging captures intermediate and high loadings, where the high-affinity fraction is already largely populated, but produces systematic deviations in the initial isotherm region.

The low-pressure residuals therefore mark the applicability boundary of the statistically equivalent single-cell approximation. This region requires a heterogeneous cell ensemble or an affinity-parameter distribution.

The model output includes x, P_i, $\langle i \rangle$, $\mathrm{Var}(i)$, and q_{calc}. These quantities identify which cell-loading states contribute in a pressure range, where the response is largest, and how rapidly the material approaches saturation. They also identify operating ranges of microporous sorbents before a larger experimental campaign.

The verification is limited to one adsorbate, one zeolite reference material, and a pressure-based thermodynamic input. The result should therefore be interpreted as a verified finite-cell formulation for the CO_2/NaY NIST RM 8850 system rather than as a universal adsorption law.

8. Conclusions

The work constructs and evaluates a finite single-cell statistical model of equilibrium adsorption in micropores using the CO_2/zeolite NaY NIST RM 8850 reference dataset. The micropore space is represented as an ensemble of statistically equivalent independent cells of finite capacity. The configurational constraint is introduced through $V_{free}(i) = v_c - i\beta$.

The finite partition function gives the main isotherm properties: monotonicity, the Henry limit, saturation, the adsorption upper bound, and the non-increase of mean loading with β. The response identity connects the derivative of the isotherm to fluctuations of cell loading and provides an internal implementation invariant. The Langmuir isotherm is obtained as an exact special case at $\omega = 1$ and $\beta = 0$.

The model separates structural quantities v_c, ω, and v_{mi} from fitted quantities K_0, E_{ads}, and β. Verification on NIST RM 8850 yields the reported fitted parameter set and the corresponding uncertainty diagnostics.

On the full dataset of 48 data points, MAE = $0.0361\,\text{mmol g}^{-1}$ and RMSE = $0.0539\,\text{mmol g}^{-1}$. In the range $p \geq 0.25$ MPa, MAE decreases to $0.0158\,\text{mmol g}^{-1}$. The Langmuir isotherm on the same full dataset gives substantially worse agreement, with MAE = $0.242\,\text{mmol g}^{-1}$.

Gas non-ideality is too small to account for the systematic residuals at $p < 0.15$ MPa. They mark the applicability boundary of the statistically equivalent single-cell approximation and identify the region where a heterogeneous cell ensemble or an affinity distribution is required.

The isotherm is represented as a consequence of a finite statistical ensemble with explicit states, probabilities, fluctuations, and response functions. Evaluation against the reference adsorption data identifies the main operating range of the single-cell approximation and its low-pressure applicability boundary.

References

1. Ruthven, D. M. Simple Theoretical Adsorption Isotherm for Zeolites. Nature Physical Science 1971, 232, 70-71. DOI: 10.1038/physci232070a0.
2. Ruthven, D. M. Principles of Adsorption and Adsorption Processes; Wiley: New York, 1984.
3. Do, D. D. Adsorption Analysis: Equilibria and Kinetics; Imperial College Press: London, 1998.
4. Wedler, C.; Ferre, A.; Azzan, H.; Danaci, D.; Petit, C.; Pini, R. Binary Adsorption Equilibria of Three CO_2 + CH_4 Mixtures on NIST Reference Zeolite Y (RM 8850) at Temperatures from 298 to 353 K and Pressures up to 3 MPa. Journal of Chemical & Engineering Data 2024, 69 (11), 4216-4229. DOI: 10.1021/acs.jced.4c00358.
5. National Institute of Standards and Technology. *Report of Investigation, Reference Material 8850, Zeolite Y*; NIST: Gaithersburg, MD, 2020.
6. Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution. Pure and Applied Chemistry 2015, 87 (9-10), 1051-1069. DOI: 10.1515/pac-2014-1117.
7. JCGM 100:2008. *Evaluation of Measurement Data: Guide to the Expression of Uncertainty in Measurement*; Joint Committee for Guides in Metrology, 2008. DOI: 10.59161/JCGM100-2008E.
8. Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. Industrial & Engineering Chemistry Fundamentals 1976, 15 (1), 59-64. DOI: 10.1021/i160057a011.