SESAMI APP: An Accessible Interface for Surface Area Calculation of Materials from Adsorption Isotherms

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Statement of need

Accurate characterization of surface area is critical for understanding a material's properties and performance. The most widely used approach to calculate a material's gravimetric surface area, i.e. surface area per unit mass, is the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938). The BET method computes the surface area of a material given the adsorption isotherm of a probe gas (i.e. N_2 or Ar) in that material. Many researchers either obtain the BET area from commercial software that comes with measurement equipment, or perform the analyses manually on a spreadsheet, which is time-consuming and nearly impossible for some types of isotherms. Furthermore, these two approaches lead to large variability in BET-calculated areas (Osterrieth et al., 2022). These challenges have motivated the development of programs for the automated and standardized calculation of BET areas (Datar et al., 2020; Iacomi & Llewellyn, 2019; Osterrieth et al., 2022; Sadeghi et al., 2020; Sinha et al., 2019).

BET theory background

The surface area of a material, S, can be calculated as

$$S = q_m N A_m, \tag{1}$$

where q_m is the molar amount of adsorbate forming a monolayer per unit mass of material, N is the Avogadro constant, and A_m is the area taken up by a single adsorbate molecule in the monolayer.

In order to attain q_m, the monolayer loading region from the isotherm can be identified using the BET equation,

$$\frac{p/p_0}{q(1-p/p_0)} = \frac{1}{q_m C} + \frac{C-1}{q_m C}\frac{p}{p_0}, \tag{2}$$

where p is the vapor pressure, p_0 is the saturation vapor pressure, q is the adsorbate loading, and C is the BET constant.

The monolayer loading region is assigned to a section of the isotherm where $\frac{p/p_0}{1-p/p_0} \cdot \frac{1}{q}$ is linear as a function of $\frac{p}{p_0}$. The linear region for BET analysis is usually chosen based on the consistency criteria proposed by Rouquerol et al. (F. Rouquerol et al., 2013; J. Rouquerol et al., 2007). The consistency criteria are as follows:

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1. The linear region should only span a range of p/p_0 values in which $q(1 - p/p_0)$ monotonically increases with p/p_0.

2. The value of C should be positive.

3. The value of the monolayer loading capacity, q_m, should correspond to a value of p/p_0 which falls within the selected linear region.

4. The value of p/p_0 calculated from BET theory, $1/(\sqrt{C} + 1)$, and p/p_0 calculated from the third consistency rule should be equal (with $\pm 10\%$ tolerance).

5. The linear region should end at the knee of the isotherm.

Once a linear region is selected, the identified uptake value is multiplied by the molecular cross-sectional area of the adsorbate, typically derived from the bulk liquid density (16.2 Å^2/molecule for N_2; 14.2 Å^2/molecule for Ar), to obtain the material's surface area, under the assumption that the adsorbate molecules only form a monolayer (Equation 1). The surface area obtained this way is referred to as the BET area.

Summary

The SESAMI web interface allows a user to make surface area calculations on their web browser simply by uploading isotherm data. The website facilitates access to the previously developed SESAMI models (SESAMI 1 and 2) for the evaluation of material's surface area (Datar et al., 2020; Sinha et al., 2019). The motivation for this interface is to lower the barrier of entry for research groups seeking to use SESAMI code, which was previously packaged in Python and Jupyter Notebook scripts.

SESAMI 1 applies computational routines to identify suitable linear regions of adsorption isotherms for BET area calculations (Fagerlund, 1973). The automated workflow includes consideration of the Rouquerol criteria and the use of coefficients of determination as a measure of linearity. Furthermore, SESAMI 1 supports a combined BET+ESW (excess sorption work) approach for linear region selection; this combined approach has been shown to outperform the BET method in some cases (Sinha et al., 2019). A user can specify a cutoff R^2 and a minimum R^2, such that a candidate linear region is favored to be selected if it has an R^2 above the cutoff, and a candidate linear region is only considered if it has an R^2 above the minimum.

SESAMI 2 applies a machine learning (specifically, regularized linear regression with LASSO) model for the accurate surface area prediction of high surface area materials, improving on BET performance for these materials (Datar et al., 2020). The LASSO model uses as input the average loading in seven isotherm pressure regions as well as pairwise products of these loadings. The SESAMI 1 and 2 routines support isotherms with N_2 and argon adsorbate at 77 K and 87 K, respectively. We note that a recent study shows that surface areas determined from N_2 and Ar isotherms are similar, despite the 2015 IUPAC report's suggested use of Ar (Datar et al., 2022; Thommes et al., 2015). In addition, the SESAMI 1 code supports isotherms with arbitrary user-specified adsorbates if temperature and adsorbate cross-section and saturation vapor pressure are specified.

The SESAMI web interface has extensive error handling and clearly alerts users of issues with their adsorption isotherm data. For example, it alerts the user if no ESW minima are found by SESAMI 1 or if the data is incompatible with SESAMI 2 code due to data sparsity in certain pressure regions. As shown in Figure 1, the interface displays SESAMI 1 calculation results including information on the chosen linear region, namely the satisfied Rouquerol criteria, the pressure range and number of data points in the region, and the coefficient of determination. The interface also displays intermediate SESAMI 1 values for surface area calculation, namely C and q_m. Furthermore, the SESAMI web interface allows the user to download figures generated by SESAMI 1 that indicate, among other things, the linear monolayer loading regions chosen by the BET and BET+ESW approaches, as well as the ESW plot (Figure 1). The user can convert output from commercial equipment to AIF format and upload the converted data to the interface for analysis. The SESAMI web interface is publicly available at https://sesami-web.org/, and source code is available at https://github.com/hjkgrp/SESAMI_web.

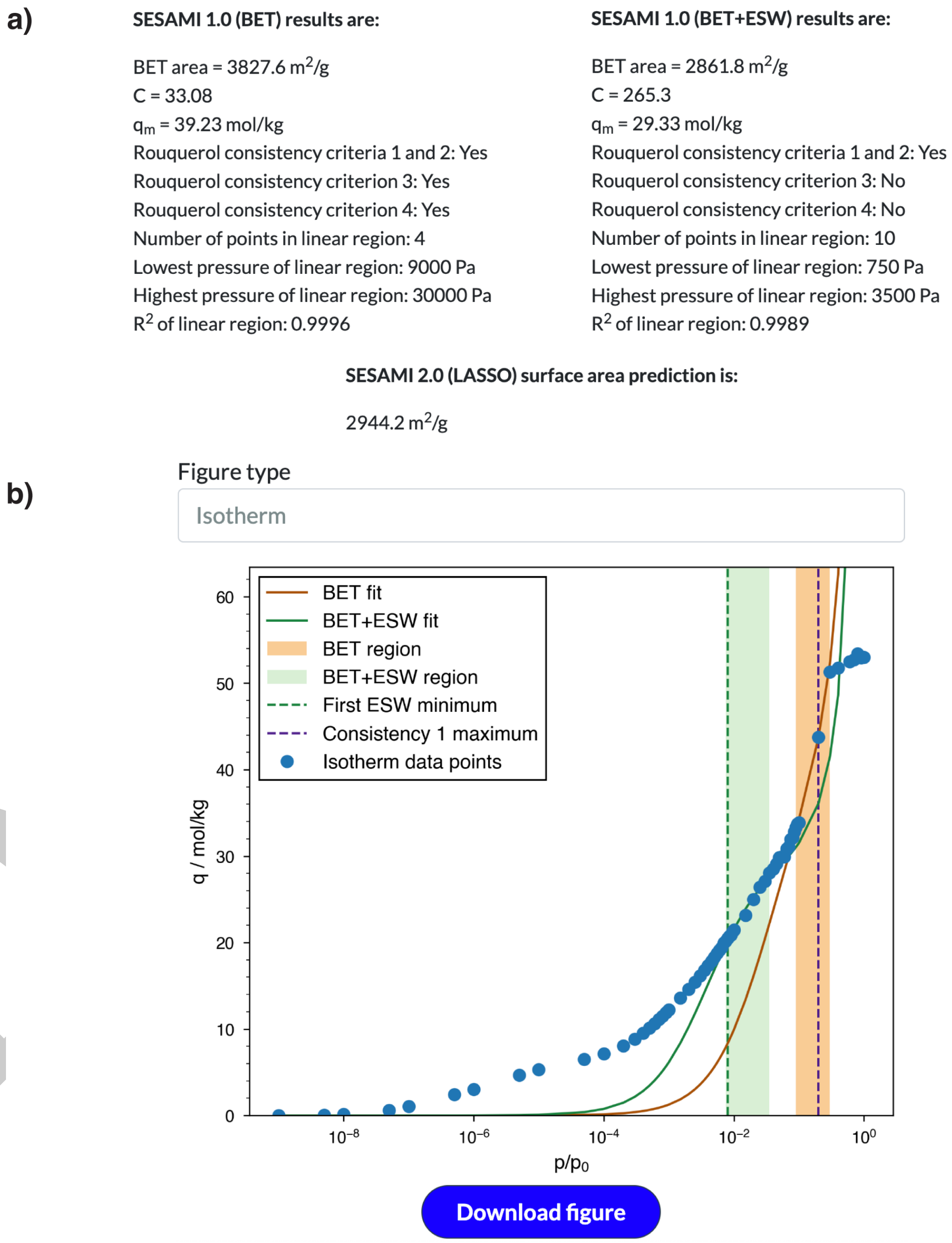

Figure 1: Information displayed by the SESAMI web interface after a calculation has been run, here for a GCMC isotherm of MIL-101. Apart from the inclusion of the LASSO prediction, default settings were used (e.g. N_2 gas). a) Interface printout of information on the SESAMI 1 chosen linear regions, and SESAMI 1 and 2 calculation results. b) Figure download functionality for figures detailing the SESAMI 1 calculation.

Benchmarking

To assess the performance of the SESAMI code in calculating surface areas from isotherms, we benchmark the SESAMI routines against other similar programs for 13 simulated and 9 experimental N_2 isotherms obtained at 77 K for 14 metal-organic frameworks (MOFs), some of which are shown in Figure 2. Simulated isotherms are obtained from grand canonical Monte Carlo (GCMC) simulations using the open-source RASPA 2.0.47 software (Dubbeldam et al., 2016), and experimental adsorption isotherms are obtained from the experimental data reported by Islamoglu and coworkers (Islamoglu et al., 2022). The isotherms are used to calculate surface areas with the SESAMI website, BETSI (Osterrieth et al., 2022; Rampersad et al., 2020), pyGAPS (Iacomi, 2019; Iacomi & Llewellyn, 2019), and BEaTmap (Sadeghi et al., 2020).

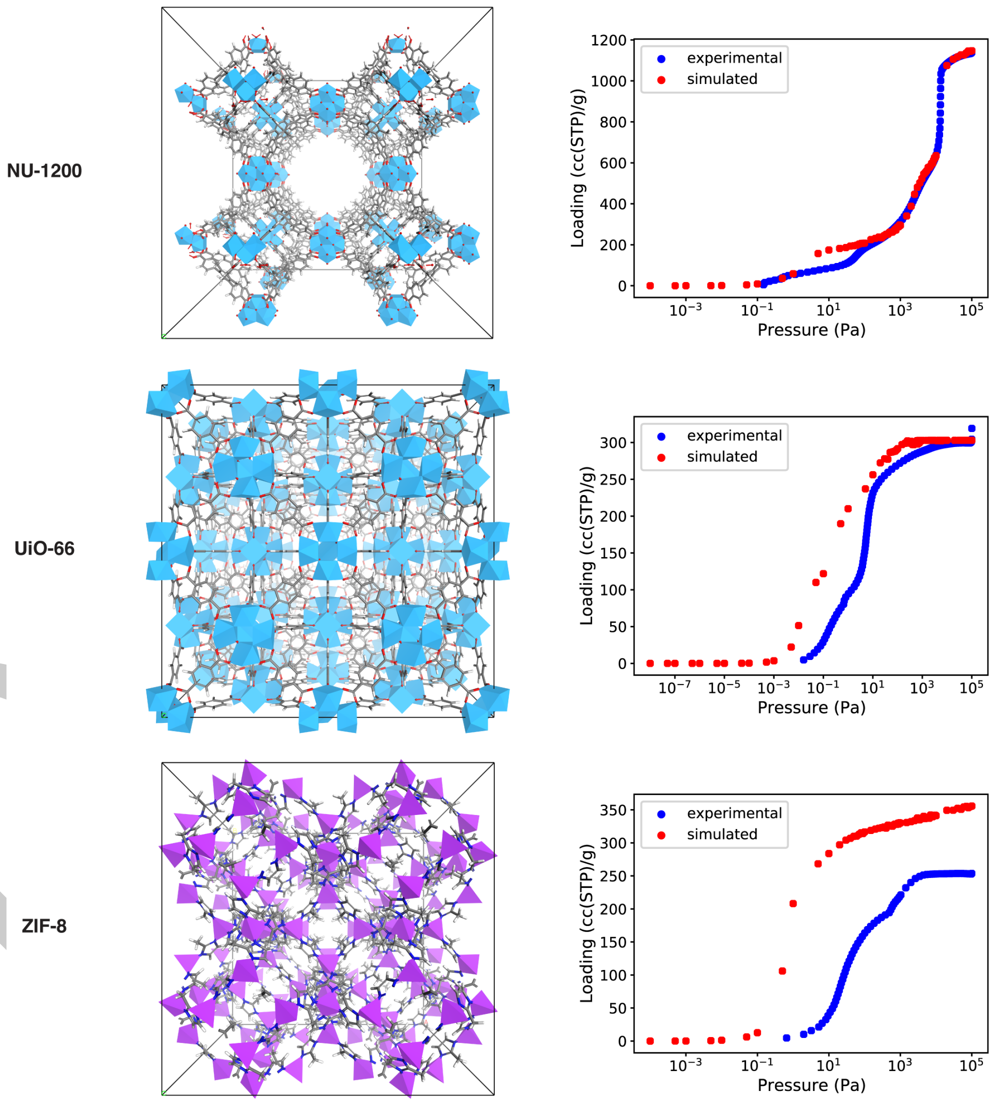

Figure 2: The crystal structures and isotherms of 3 of the 14 MOFs used to benchmark different isotherm to surface area codes.

We find that over the set of 13 GCMC isotherms, the SESAMI machine learning model (run from the web interface) and BEaTmap have the best correlation with Zeo++ version 0.3

surface areas (Willems et al., 2012) calculated with a 1.67 Å radius probe N_2 molecule (Table 1 and Table 2). Differences in performance across software on this benchmark set can be attributed to the differing implementations of linear region identification, or in the case of the SESAMI machine learning model, fundamental differences in how the software calculate surface areas. Nevertheless, all software are in generally good agreement, underscoring the benefit of a computational approach to surface area calculation. The agreement between software is also not surprising due to the similar approach taken by most of the codes of considering multiple subsets of consecutive data points and applying checks like the Rouquerol criteria to select a linear region for BET analysis (SESAMI 1, BETSI, BEaTmap). The agreement between software is also observed over the 9 experimental isotherms (Table 3).

The CIF files used to generate GCMC isotherms, benchmark isotherms, XLSX files of calculated surface areas across different software tools for both GCMC and experimental isotherms, detailed settings used for each software, and analysis scripts employed are available at https://github.com/hjkgrp/SESAMI_web. Software settings are also reported in Table 4. When a software for isotherm to surface area calculation does not find a surface area, the reason can vary from no ESW minimum being found or no suitable linear region containing an ESW minimum being found in the case of SESAMI 1 (BET+ESW), to an insufficient number of data points in the chosen BET region in the case of pyGAPS.

Table 1: Calculated surface areas (m^2/g) for the 13 MOFs with GCMC isotherms. Cases where a software does not find a surface area are denoted by N/A. Zeo++ calculations are conducted with the same CIF files used to generate GCMC isotherms, and a 1.67 Å radius probe N_2 molecule, the high accuracy flag, and 2,000 Monte Carlo samples per atom are used. All other software take as input the GCMC isotherms.

	SESAMI 1 (BET)	SESAMI 1 (BET+ESW)	SESAMI 2 (LASSO)	BETSI	py-GAPS	BEaTmap	Zeo++
HKUST-1	2001	1933	2089	1962	1902	1980	2397
IRMOF-1	3502	3543	3123	3519	3504	N/A	3722
MIL-100 (Cr)	2107	1853	2111	N/A	1852	2094	1957
MIL-100 (Fe)	2386	2438	2203	2426	82	2423	1933
MIL-101	3828	2862	2944	N/A	2939	3331	3164
MIL-53 (Al)	1221	1168	1405	1164	1183	1212	1510
MOF-74 (Mg)	1828	1834	1902	N/A	1839	1791	1796
MOF-808	44	N/A	1275	N/A	N/A	1147	1690
NU-1000	2439	2181	2633	N/A	2144	2672	3050
NU-1200	2711	934	2601	N/A	1073	2930	3192
NU-1500 (Fe)	3543	3594	3111	N/A	3758	3492	3944
UiO-66	1239	1239	1443	N/A	1242	1304	1289
ZIF-8	1429	1386	1575	1381	1390	1414	1588

Table 2: Comparison between calculated surface areas from software for isotherm to surface area calculation and from Zeo++, over the 13 MOFs with GCMC isotherms. The mean absolute percent error and Pearson correlation coefficient are taken with respect to Zeo++ calculations for each software, over all successful surface area calculations for that software.

Software	Mean absolute percent error (MAPE)	Pearson correlation coefficient	Successful calculations (out of 13)
SESAMI 1 (BET)	19.4	0.85	13
SESAMI 1 (BET+ESW)	17.9	0.72	12
SESAMI 2 (LASSO)	12.4	0.95	13
BETSI	17.0	0.92	5
pyGAPS	23.0	0.75	12
BEaTmap	12.6	0.93	12

Table 3: Calculated surface areas (m^2/g) for the 9 MOFs with experimental isotherms. Cases where a software does not find a surface area are denoted by N/A. All software take as input the experimental isotherms.

	SESAMI 1 (BET)	SESAMI 1 (BET+ESW)	SESAMI 2 (LASSO)	BETSI	py-GAPS	BEaTmap
HKUST-1	1505	1466	1668	N/A	1495	1498
MOF-74 (Mg)	1580	1467	1692	N/A	1574	1565
MOF-808	1998	900	1727	N/A	2439	1752
NU-1000	2154	2090	2385	N/A	2654	2459
NU-1200	2893	2718	2781	2758	3917	3069
NU-1500 (Fe)	3305	3409	2809	N/A	3413	3227
SIFSIX-3 (Ni)	356	201	716	N/A	355	353
UiO-66	1251	1228	1413	1250	1249	1246
ZIF-8	1092	910	1214	N/A	1082	1047

Table 4: Settings used for software for isotherm to surface area calculation. All BET calculations by SESAMI 1 and pyGAPS reported in this work fulfill Rouquerol criteria 1 and 2. SESAMI 1 code requires at least 4 points for the linear region, while pyGAPS requires at least 3.

Software	Mode of access	Settings
SESAMI 1 (BET) SESAMI 1 (BET+ESW) SESAMI 2 (LASSO)	Run from SESAMI web interface Accessed February 2023	Type of gas: Nitrogen Custom adsorbate: No Scope: BET and BET+ESW R^2 cutoff: 0.9995 R^2 min: 0.998 Include ML prediction?: Yes

Software	Mode of access	Settings
BETSI	GUI started from the command line GitHub version 1.0.20	Minimum number of points in the linear region: 10 Minimum R^2: 0.998 Rouquerol criteria 1: Yes Rouquerol criteria 2: Yes Rouquerol criteria 3: No Rouquerol criteria 4: No Rouquerol criteria 5: No
pyGAPS	Python package Conda version 4.4.2	Used function `area_BET` Default values for keyword arguments
BEaTmap	Run from BEaTmap web interface Accessed February 2023	Adsorbate cross-sectional area: 16.2 $Å^2$/molecule Criteria 1: Yes Criteria 2: Yes Criteria 3: No Criteria 4: No Minimum number of data points: 5 BET calculation criteria: Maximum data points

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