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SESAMI Web: An Accessible Interface for Surface Area Prediction of Materials from Adsorption Isotherms

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Statement of need

Surface area determination is important for the evaluation of a porous material's viability in applications ranging from catalysis to separations to gas storage. The most widely used approach for the evaluation of a material's specific surface area, i.e. surface area per unit mass, is the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938). That is, given the adsorption isotherm of a gas (i.e., N_2 or Ar) in an adsorbent, one can use the BET theory to determine the specific surface area of the adsorbent upon identification of an appropriate linear region in the isotherm. This procedure is sometimes automatically performed by the software program that comes with the commercial adsorption apparatus that measures the adsorption isotherm. Unfortunately, the linear region selection is a large source of variability in BET-calculated areas. In addition, for certain types of isotherms, automatic selection of the linear region by the commercial software sometimes fails. As a result, many researchers perform the analyses manually on a spreadsheet, which can become time-consuming and nearly impossible for some types of isotherms (Osterrieth et al., 2022). These challenges have motivated the development of programs for the automated determination of BET areas (Datar et al., 2020; Iacomi & Llewellyn, 2019; Osterrieth et al., 2022; Sadeghi et al., 2020; Sinha et al., 2019). Furthermore, shortcomings of BET as a tool for surface area calculation, such as its relatively poor performance in treating high surface area materials with multimodal pore sizes (Gómez-Gualdrón et al., 2016; Wang et al., 2015), have led to the development of alternate methods for surface area calculation from isotherms (Datar et al., 2020; Sinha et al., 2019).

Summary

In contrast to previously developed programs which require use of the command line (Iacomi & Llewellyn, 2019; Osterrieth et al., 2022) and familiarity with Python (Datar et al., 2020; Iacomi & Llewellyn, 2019; Sinha et al., 2019), the SESAMI web interface allows a user to make surface area predictions on their web browser simply by uploading isotherm data. The website facilitates access to the previously developed SESAMI models (SESAMI 1 and 2) for porous material surface area prediction (Datar et al., 2020; Sinha et al., 2019) and has been tested by experimental groups. 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 surface area predictions (Fagerlund, 1973). The automated workflow includes consideration of Rouquerol criteria (F. Rouquerol et al., 2013; J. Rouquerol et al., 2007) 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 approach 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. On the other hand, 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 routines support isotherms with N_2 and argon adsorbate at 77 K or 87 K, respectively. We note that a recent study shows that surface areas determined from N_2 or Ar isotherms are similar, despite the latest 2015 IUPAC report's suggested use of Ar (Datar et al., 2022).

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 is 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 (F. Rouquerol et al., 2013; J. Rouquerol et al., 2007), 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 the BET constant, C, and the monolayer adsorption loading, q_m. Furthermore, the SESAMI web interface allows the user to download figures generated by SESAMI 1 that indicate, among other things, the chosen linear monolayer loading regions by the BET and BET+ESW approaches as well as the excess sorption work 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.

a)

SESAMI 1.0 (BET) results are:

BET area = 2430.9 m^2/g
C = 201.1
q_m = 28.42 mol/kg
Rouquerol consistency criteria 1 and 2: Yes
Rouquerol consistency criterion 3: Yes
Rouquerol consistency criterion 4: Yes
Number of points in linear region: 9
Lowest pressure of linear region: 3500 Pa
Highest pressure of linear region: 8000 Pa
R^2 of linear region: 0.9996

SESAMI 1.0 (BET+ESW) results are:

BET area = 2346.7 m^2/g
C = 248.1
q_m = 27.44 mol/kg
Rouquerol consistency criteria 1 and 2: Yes
Rouquerol consistency criterion 3: No
Rouquerol consistency criterion 4: Yes
Number of points in linear region: 9
Lowest pressure of linear region: 600 Pa
Highest pressure of linear region: 1500 Pa
R^2 of linear region: 0.9985

SESAMI 2.0 (LASSO) surface area prediction is:

2099.1 m^2/g

b)

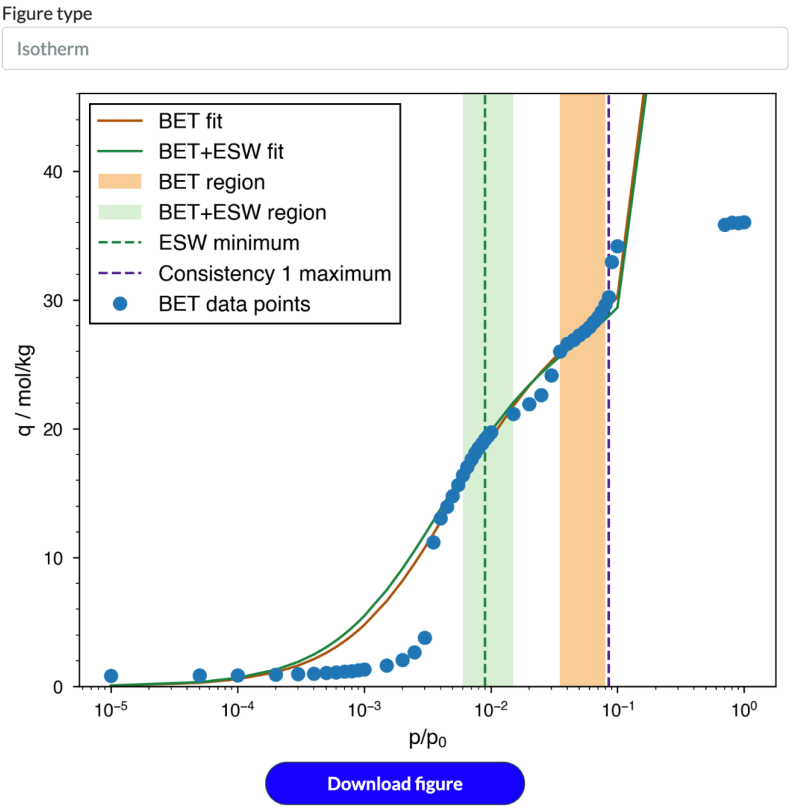

Figure 1: Information displayed by the SESAMI web interface after a calculation has been run. a) Interface printout of information on the SESAMI 1 chosen linear regions, and SESAMI 1 and 2 calculation results. b) Figure download functionality for figures detailing SESAMI 1 calculation.

Benchmarking

To assess the performance of the SESAMI code in predicting 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 software (Dubbeldam et al., 2016), and experimental adsorption isotherms are obtained from the experimental data reported by

Islamogu and coworkers (Islamoglu et al., 2022). The data are then used to calculate the surface areas from the SESAMI website, BETSI (Osterrieth et al., 2022; Rampersad et al., 2020), pyGAPS (Iacomi, 2019; Iacomi & Llewellyn, 2019), and BEaTmap (Sadeghi et al., 2020).

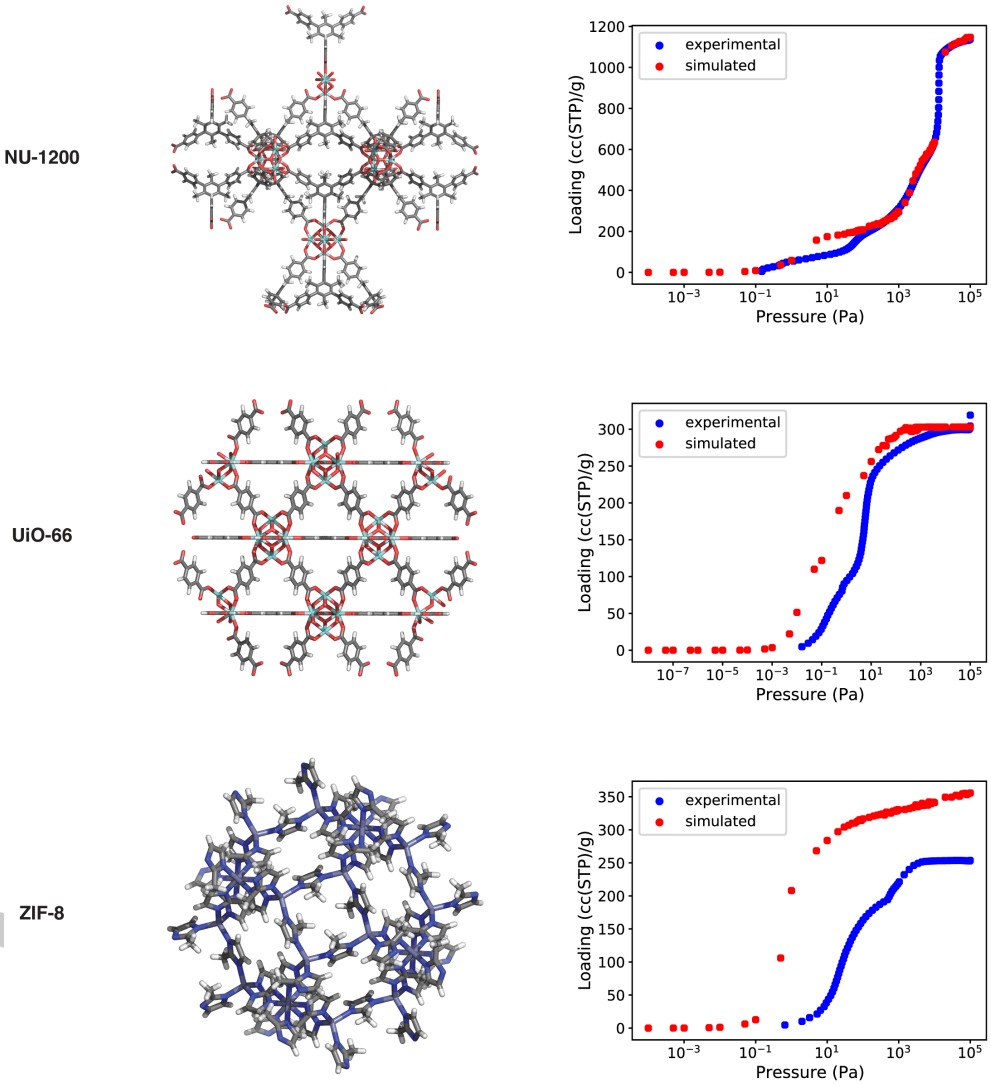

Figure 2: The crystal structures and isotherms of 3 of the 14 MOFs used to benchmark different isotherm to surface area codes.

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++ surface areas (Willems et al., 2012) calculated with a 1.67 Å probe N_2 molecule (Tables 1 and 2). 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. Indeed, this agreement is also observed over the 9 experimental isotherms (Table 3). The benchmark isotherms, XLSX files of surface area predictions 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.

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 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 surface area predictions from Zeo++ and software for isotherm to surface area calculation, over the 13 MOFs with GCMC isotherms. The number of successful isotherm to surface area calculations for each software are indicated as well.

Surface area calculation software	Mean Absolute Percent Error (MAPE)	Pearson correlation coefficient	Successful calculations
SESAMI 1 (BET)	19.4	0.85	13
SESAM1 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 other 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

	SESAMI 1 (BET)	SESAMI 1 (BET+ESW)	SESAMI 2 (LASSO)	BETSI	py-GAPS	BEaTmap
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.

Surface area calculation software	Mode of access	Settings
SESAMI 1 (BET) SESAM1 1 (BET+ESW) SESAMI 2 (LASSO)	Run from SESAMI web interface	Type of gas: Nitrogen Scope: BET and BET+ESW R^2 cutoff: 0.9995 R^2 min: 0.998 Include ML prediction?: Yes
BETSI	GUI started from the command line	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	Used function `area_BET` Default values for keyword arguments
BEaTmap	Run from BEaTmap web interface	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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