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Correlated-Cell Model for Small-Angle X-Ray Scattering of Supported-Metal Catalysts and Other Amorphous Systems

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For amorphous multiphase systems, a model based on the division of space into cells, each of which is filled with one phase or another on a random basis, has been shown useful. We here propose an improvement, which allows for correlations between the contents of neighboring cells, and apply it to samples of SiO_2, Al_2O_3, and catalysts using SiO_2 and Al_2O_3 as supports. Compared to the uncorrelated-cell model, the predicted scattering intensities fit the measured intensities significantly better. The value determined for the additional correlation parameter indicates an enhanced tendency for neighboring cells to contain the same phase. Interphase surface areas are derived and compared with other measurements. The additional parameter does not suffice to define all the surfaces for a system of more than two phases; an additional assumption is required.

I. INTRODUCTION

In principle, the small-angle X-ray scattering (SAXS) from amorphous systems such as supported-metal catalysts can give information about the interphase surface areas. If such a system is modeled as a dispersion of internally homogeneous (uniform electron density) phases with sharp interphase boundaries, the scattering intensity may be written (*1*) as the Fourier transform of the correlation function

$$\gamma(r) = 1 - \frac{\sum_{ij} P_{ij}(r)(n_i - n_j)^2}{\sum_i \phi_i(n_i - \bar{n})^2} \qquad (1)$$

Here $P_{ij}(r)$ is the probability (*2*) that a line segment of length r within the sample has one end in phase i and the other in phase j; $P'_{ij}(0)$ may be shown (*2, 3*) to be equal to $S_{ij}/4V$, where S_{ij} is the surface area between phases i and j. In Eq. (1), n_i is the electron density of phase i, ϕ_i the volume fraction of phase i, and

$$\bar{n} = \sum_i \phi_i n_i$$

is the average electron density. Measurements of SAXS intensity as a function of scattering angle give only $\gamma(r)$, whereas surface areas require knowledge of the $P_{ij}(r)$. Although some necessary properties of the $P_{ij}(r)$ are known, it is impossible to obtain individual $P_{ij}(r)$ from $\gamma(r)$ without invoking a model or additional assumptions (except for a two-phase system, for which there is only one independent P_{ij} function).

Recently, we have proposed (*4*) cell models for these systems, in which the system is modeled by dividing space into cells and filling each with one phase or another. In the simplest cell model, each cell is filled with one of the phases with probability equal to the (known) volume fraction. In this case, it can be shown (*5*) that

$$P_{ij}(r) = \phi_i \delta_{ij} p_0(r) + \phi_i \phi_j (1 - p_0(r)) \qquad (2)$$

where $p_0(r)$ is the noncrossing function, the probability that a length r lies wholly within one cell. Then $\gamma(r)$ becomes just $p_0(r)$. Improved cell models, in which the metal and support occupy cells of different average size, have also been developed.

The random filling of the cells in these models makes the joint probability, that one of two neighbor cells be filled with phase i

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and the other with phase j, just the product of volume fractions $\phi_i\phi_j$. Considerations such as surface tension suggest that the probability that neighboring cells contain the same phase should be enhanced relative to random distributions. The model proposed below allows the joint probability to differ from $\phi_i\phi_j$. Applying the model to several amorphous two-phase and three-phase systems, we consider the effect of the additional parameter on the fit obtained, and on the derived interphase surface areas.

The theory of this model is given in Section II. In Section III we show results of its application to four systems, comparing with the uncorrelated-cell model of Eq. (2). Discussion and evaluation of the model follows in Section IV.

II. THEORY

The theory of the correlated-cell model will now be presented. In can be anticipated that the probability that the neighbors of a cell containing phase j also contain this phase is different (probably higher) than the average probability (volume fraction ϕ_j). An additional parameter, representing this neighbor-cell correlation, should enter the correlation function. Let ψ_{ij} be the conditional probability that, given a cell containing phase j, a nearest-neighbor cell contains phase i. Two cells are said to be neighbors if they share a cell boundary (face). Because of their definition, the conditional probability ψ_{ij} obey

$$\psi_{ji}\phi_i = \psi_{ij}\phi_j \tag{3}$$

either expression simply representing the probability that, given two neighboring cells, one contains phase i and the other phase j. Correlations between the contents of cells which are not neighbors are not considered in this model. Since the overall volume fractions of the phases are given, the ψ_{ij} must obey the normalization condition

$$\sum_j \psi_{ij}\phi_j = \phi_i = \sum_j \psi_{ji}\phi_i$$

where (3) has been used. Thus

$$\sum_j \psi_{ji} = 1. \tag{4}$$

Since for an N-phase system there are $\frac{1}{2}N(N-1)$ conditions (3) and N conditions (4), there are $\frac{1}{2}N(N-1)$ independent ψ_{ij}, the same as the number of independent $P_{ij}(r)$.

The correlation function now involves $p_1(r)$, the nearest-neighbor crossing function: $p_1(r)$ is the probability that a stick of length r, randomly thrown into the system, has its two ends in nearest-neighbor cells. According to the assumptions of this model,

$$P_{ij}(r) = p_0(r)\phi_i\delta_{ij} + p_1(r)\psi_{ji}\phi_i + [1 - p_0(r) - p_1(r)]\phi_i\phi_j \tag{5}$$

instead of (2). If we insert this into (1), we find for the correlation function, after some algebraic manipulation,

$$\gamma(r) = p_0(r) + p_1(r)\left[1 - \sum_{ij} \psi_{ji}\phi_i(n_i - n_j)^2 \Big/ \sum_{ij} \phi_i\phi_j(n_i - n_j)^2\right]. \tag{6}$$

For a two-phase system, this reduces to

$$\gamma(r) = p_0(r) + p_1(r)[1 - \tfrac{1}{2}(\psi_{21}/\phi_2) - \tfrac{1}{2}(\psi_{12}/\phi_1)]$$

where the two terms in parentheses are identical. If $\psi_{ji} = \phi_j$, $\gamma(r)$ reduces to the random-filling results, $\gamma(r) = p_0(r)$.

It is necessary now to consider the function $p_1(r)$. Although an expression for $p_1(r)$ is not known to us, we can state several conditions which it must obey: (a) $p_1(r)$ must always lie between 0 and 1, being a probability. (b) $p_1(0) = 0$ since a stick of length 0 must lie wholly within one cell. (c) $p_1(\infty) \rightarrow 0$ since for large distance the probability of crossing only one cell boundary approaches zero. (d) $(dp_1/dr) = -(dp_0/dr)$ at $r = 0$ since a stick of length dr can cross no more than one cell boundary. (e) The integral of $p_1(r)$ over all space must yield the average volume of all neighbor cells of an arbitrary cell, i.e., $\overline{NV_c}$ where N is the number of nearest neighbors of a cell and V_c the volume of a cell. The last condition follows from the definition of $p_1(r)$ as the probability that end B of a length r lies in a cell which is a neighbor to the cell in which end A is found. We expect $p_1(r)$ to be nonoscillatory, passing through a single maximum. We use these conditions to construct a function $p_1(r)$. The actual $p_1(r)$, unless it has oscillations or other unexpected features, should look essentially like this function.

The most successful of our cell models (*6*) have used the Voronoi tessellation (*7*) to construct these cells, and this is used in the correlated-cell model. The Voronoi construction starts from a random distribution of points of average density c (Poisson points). Bisecting the lines connecting each point to the others by planes, one assigns to each Poisson point the volume bounded by the planes closest to it. The properties of these volumes (Voronoi cells) have been studied (*8*), and the noncrossing function $p_0(r)$ calculated (*6, 9*). Our procedure is to calculate intensities for comparison with experiment, for which we require the slit-smeared Fourier transform:

$$\tilde{I}_t(h) = 2\int_0^\infty I_t(\sqrt{(h^2 + s^2)})ds \qquad (7a)$$

$$I_t(h) = 2\pi\int_0^\infty (hr)^{-1}(\sin hr)\gamma(r)r^2dr. \qquad (7b)$$

This procedure has been carried out for $p_0(r)$ and the results tabulated; we write $\tilde{I}_t(h)$ as $4\pi l^2F(hl)$, where $l = (\pi c/4)^{-1/3}$.

Referring to condition (e), we approximate the average of NV_c by the product of the average number of neighbor cells (15.54 for the Voronoi construction) and the average cell volume ($1/c$).

$$\int_0^\infty 4\pi r^2p_1(r)dr = 15.54c^{-1} = 15.54(4l/\pi)^3. \qquad (8)$$

We now assume the algebraic form

$$p_1(r) = Kre^{-pr^\alpha} \qquad (9)$$

which satisfies conditions (a), (b), and (c), and use the remaining conditions to fix the parameters K, p, and α. The initial slope condition (d) means that

$$K(1 - \alpha pr^\alpha)_0 = -(dp_0/dr)_0 = \frac{8}{9}\left(\frac{9\pi c}{16}\right)^{1/3}\Gamma\left(\frac{2}{3}\right) = 1.45522c^{1/3} \qquad (10)$$

where the small-r form of the Voronoi noncrossing function has been used. From condition (e) or Eq. (8):

$$K\int_0^\infty r^3e^{-pr^\alpha}\,dr = \frac{K(4/\alpha)!}{4p^{4/\alpha}} = 15.54/(4\pi c). \qquad (11)$$

It is not possible to determine all three parameters; for simplicity in Fourier transforming we take $\alpha = 1$ so $K = 1.45522c^{1/3}$ and, from (11), $p = 1.63008c^{1/3}$.

Now $\gamma(r)$ is constructed using (6) and (9). On Fourier transforming and slit smearing $\gamma(r)$, we find, for a two-phase system,

$$\tilde{I}_t(h) = 4\pi l^2F(hl) + 4\pi^2K(1 - \psi_{21}/\phi_2)(5.3144c^{2/3} - h^2)(2.6572c^{2/3} + h^2)^{-5/2}$$

where the first term is the intensity corresponding to $p_0(r)$ for a Voronoi cell density c and characteristic length $l = (\pi c/4)^{-1/3}$. This may be rewritten as

$$\tilde{I}_t(h) = l^2[4\pi F(hl) + 62.267(1 - \psi_{21}/\phi_2)(6.2430 - h^2l^2)(3.1215 + h^2l^2)^{-5/2}]. \qquad (12)$$

For a multiphase system, the factor $(1 - \psi_{21}/\phi_2)$ is replaced by

$$D = 1 - \sum_{ij}\psi_{ji}\phi_i(n_i - n_j)^2 \Big/ \sum_{ij}\phi_i\phi_j(n_i - n_j)^2. \qquad (13)$$

The scattering intensity is $C\tilde{I}_t(h)$, where

$$C = \overline{\eta^2}VI_e(h)$$

with $\overline{\eta^2}$ the mean-square electron-density fluctuation, V the illuminated volume, and $I_e(h)$ the Thomson cross section, which may be taken as a constant for our range of

h. If absolute intensities are not measured, as in our experiments, C becomes a fitting parameter. We vary three parameters (C, l, and D) to minimize the quantity

$$q = \sum_i (\tilde{I} - \tilde{I}_t)_i^2/\tilde{I}_i N_I \qquad (14)$$

where $\tilde{I}_i$ is the intensity measured for $h = h_i$ and N_I is the number of values of h for which intensity is measured.

According to Eq. (6), the interphase surface areas are given by

$$\begin{aligned} S_{ij}/4V &= (\psi_{ji}\phi_i - \phi_i\phi_j)p_1'(0) - \phi_i\phi_j p_0'(0) \\ &= \psi_{ji}\phi_i p_1'(0) \qquad (15) \end{aligned}$$

since $p_1'(0) = -p_0'(0)$ (condition (d), above). It has been shown that $p_0'(0) = -1.57724/l$, and

$$S_{ij}/V = \tfrac{1}{2}(\psi_{ji}\phi_i + \psi_{ij}\phi_j)6.3090/l. \qquad (16)$$

By fitting intensities, we can derive a value for D (Eq. (12)), but not for the individual ψ_{ij}, except for a two-phase system. This means that the individual interphase surfaces cannot be obtained for multiphase systems without additional assumptions, as discussed in Section IV. For a two-phase system, γ is simply $1 - P_{12}/\phi_1\phi_2$, so that the surface area is given by

$$S_{ij}^{(2)}/V = -4\phi_1\phi_2\gamma'(0). \qquad (17)$$

Furthermore, the value of $\gamma'(0)$ is given, in general, by (*2*)

$$\gamma'(0) = -[\lim_{h\to\infty} h^3\tilde{I}(h)] \Big/ \int_0^\infty h\tilde{I}(h)dh \qquad (18)$$

so that S_{12} for a two-phase system is available with no need for a model beyond the assumption of uniform phases with discontinuous changes in electron density at boundaries.

III. EXPERIMENTAL

The correlated-cell theory was applied to SAXS measurements on four samples: SiO_2, Pt/SiO_2, Al_2O_3, Pt/Al_2O_3.[1] The volume fractions are given, with other properties of the system, in Table 1. Surface areas for these samples, obtained by subtraction of support scattering, have been reported (*10*). Our measurements were made with a position-sensitive detector in the infinite-slit geometry. For experimental details, see Ref. (*11*).

For the SiO_2, fitting intensities by minimizing q with respect to the three parameters D, l, and C, we find $l = 89.06$ and $1 - \psi_{21}/\phi_2 = 0.0549$. The value of q is 55, to be compared with a value of 112 obtained with no intercell correlation. The additional parameter thus significantly improves the fit. The initial slope of the correlation function

TABLE I

Characterization of Catalyst Samples

Sample	Mass density	Volume fractions[a]			Electron densities[a,b]		
		ϕ_1	ϕ_2	ϕ_3	n_1	n_2	n_3
SiO_2	0.3843	0.1755	0.8245	0.0	1.093	0.0	—
SiO_2 + Pt	0.3882	0.17544	0.8242	0.00036	1.093	0.0	8.576
Al_2O_3	0.6486	0.1753	0.8247	0.0	1.814	0.0	—
Al_2O_3 + Pt	0.6638	0.17509	0.82372	0.00118	1.814	0.0	8.576

[a] Phase 1 = support, phase 2 = void, phase 3 = metal.

[b] In moles of electrons per cubic centimeter.

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[1] The samples were kindly supplied and characterized by Dr. J. Cohen and co-workers. The volume fractions were obtained from density measurements.

is

$$\gamma'(0) = (-1.57724/l) + (1 - \psi_{21}/\phi_2)(1.57724/l) = -0.01674 \quad (19)$$

which is essentially the value determined directly from the experimental data according to (18), −0.0166 ± 0.0008. The uncorrelated-cell model gives $\gamma'(0) = -0.01662$. The value of ψ_{21} implies a small tendency for cells filled with SiO_2 to have neighbors also containing SiO_2, which is physically reasonable. The length l is about 6% smaller than for the uncorrelated-cell model, which gave $l = 94.89$: smaller cells plus positive intracell correlations tend to keep the average size of the pieces of silica the same in both models.

For the three-phase system Pt/SiO_2, Eq. (6) becomes

$$\gamma(r) = p_0(r) + p_1(r)(1 - 1.0580\psi_{21} - 49.590\psi_{31} - 306.00\psi_{32}). \quad (20)$$

Three parameters are to be varied in minimizing the deviation between experimental and theoretical scattering intensities, just as for the two-phase system. The best value of q, 63, is obtained with a characteristic cell length of 86.73 Å and a value of 0.0952 for the quantity in parenthesis in (20). (The uncorrelated-cell model with $l = 95.21$ Å gives $q = 173$.) There is thus again a slight positive correlation between cells (enhanced probability for neighbor cells to have the same contents). The slope $\gamma'(0)$ is −0.01738 ± 0.00055 from the data via (18), −0.01645 from (19), and −0.01657 from the uncorrelated-cell model.

For Al_2O_3, the correlated-cell model, with a three-parameter fitting function, gives $q = 42$. The characteristic length is found to be 83.54 and the correlation parameter $1 - \psi_{21}/\phi_2$ is 0.1695, representing somewhat more correlation between cells than for SiO_2. The uncorrelated Voronoi, with two parameters, gave $q = 84$ with $l = 91.48$. The correlated Voronoi gives $\gamma'(0) = -0.01568$, which is considerably closer to $\gamma'(0)$ from (18), −0.01596, than is the uncorrelated Voronoi result, −0.01724. As reflected in the decreased q, the correlation factor is a significant improvement in the model.

Fitting the Pt/Al_2O_3 catalyst scattering to a Voronoi function gives $l = 81.3$, $q = 235$, $\gamma'(0) = -0.01940$. Introduction of a correlation factor reduces q to 170 with $l = 72.7$ Å and the correlation coefficient D equal to 0.2033. Again there is a positive correlation between contents of neighboring cells. The correlated Voronoi gives $\gamma'(0) = -0.01731$, while the catalyst scattering gives $-\gamma'(0) = 0.02043 \pm 0.0011$ according to (18). The discrepancy between $\gamma'(0)$ values comes about because minimization of q in this case produces a curve which is close to $\tilde{I}$ for the smallest h values, but lies below it for the second half of the h range. This sample thus differs from the others with respect to our model.

IV. DISCUSSION

The correlated Voronoi cell model seems to be an improvement over uncorrelated cells: q decreases significantly in every case when the correlation factor is introduced, and $\gamma'(0)$ is improved or essentially the same, except for Pt/Al_2O_3. This suggests that it represents a better description of the way in which the phases are distributed. In physical terms, there seems to be a tendency for adjacent cells to be filled with the same material.

Of course, q will decrease whenever additional parameters become available for fitting the intensities. To judge whether the decrease is significant, and to compare models with different numbers of parameters, we consider a figure of merit F which is a generalization of that used for linear least-squares analyses (*13*). We first define the dimensionless quantity

$$R^2 = 1 - \frac{\sum_j (\tilde{I}_j - I_{tj})^2/\tilde{I}_j}{\sum_j |\tilde{I}_j - \bar{I}|} = 1 - \frac{N_I q}{\sum |\tilde{I}_j - \bar{I}|}$$

where N_I = number of evaluation points

TABLE 2

Comparison[a] of Models

System	$\bar{I}$	Uncorrelated cells			Correlated cells		
		q	R^2	$F/1000$	q	R^2	$F/1000$
SiO_2	24669	112	0.99678	6.64	55	0.99842	8.82
Pt/SiO_2	27040	173	0.99532	4.47	63	0.99830	8.01
Al_2O_3	31144	84	0.99808	11.19	42	0.99904	14.58
Pt/Al_2O_3	49798	235	0.99655	6.20	170	0.99750	5.59

[a] $R^2 = 1 - Nq/\Sigma|\bar{I}_k - \bar{I}|$, where $\bar{I}$ is average intensity, N = number of measurements. Figure of merit $F = [R^2/(1 - R^2)](N - K - 1)/K$, where K = number of parameters (2 for uncorrelated cells, 3 for correlated cells).

(intensities) and $\bar{I}$ = mean intensity, i.e., $N_1\bar{I} = \Sigma\bar{I}_j$. Then we write

$$F = \frac{R^2}{1 - R^2}\frac{N - K + 1}{K} \tag{21}$$

where K is the number of parameters ($K = 2$ for uncorrelated cells, $K = 3$ for correlated cells). For fixed K, F becomes larger the better the fit, but for fixed R^2, F decreases as K increases, becoming zero if $K = N - 1$. Calculations of R^2 and K for the two models applied to the four samples give the results of Table 2. For SiO_2, Pt/SiO_2, and Al_2O_3, F increases significantly when the cell correlation parameter is put in, by factors of 1.3, 1.8, and 1.3. However, F decreases slightly for Pt/Al_2O_3, confirming our suspicion that the correlated-cell model is not a particularly good one in this case.

For a two-phase system (SiO_2 or Al_2O_3) the interphase surface area is given by

$$S/V = -4\phi_1\phi_2\gamma'(0) \tag{22}$$

independently of any model. Thus, the correlated-cell model's utility here is for its physical picture, since it is not needed for the determination of surface area. We find $S/V = 0.00967$ Å^{-1} = 96.7 m^2/cm^3 for SiO_2 and $S/V = 0.00923$ Å^{-1} for Al_2O_3, using $\gamma'(0)$ obtained from the data via (18). Dividing by the mass densities, we obtain specific surfaces of 252 and 142 m^2/g, respectively. Table 3 gives specific surfaces calculated using the cell models. Nandi *et al.* (*10*) have reported surface areas of 327 and 222 m^2/g from their SAXS measurements on these systems. Their BET measurements yielded 285 and 160 m^2/g, significantly closer to our SAXS results.

To obtain surfaces for a multiphase sys-

TABLE 3

Surface Areas in Å^{-1} (Above) and in m^2/g (Below)

	Pt/SiO_2			Pt/Al_2O_3		
	S_{12}	S_{13}	S_{23}	S_{12}	S_{13}	S_{23}
Uncorrelated cells	0.00958	4.2×10^{-6}	19.7×10^{-6}	0.01119	16.0×10^{-6}	75×10^{-6}
	247.	0.108	0.51	169.	0.241	1.13
Correlated cells[a]	0.00952	4.2×10^{-6}	19.5×10^{-6}	0.00997	14.2×10^{-6}	67×10^{-6}
	245.	0.108	0.50	150.	0.214	1.01

[a] Using Eq. (24).

tem, knowledge of the correlation function does not suffice; a model is required to extract the $P_{ij}(r)$ from $\gamma(r)$. One can also derive S_{12} by subtraction of the scattering of the unmetallized support from that of the catalyst, making several assumptions (*12*), which may not be justified (*11*). Nandi *et al.* (*10*) report 324 and 217 m^2/g for SiO_2 and Al_2O_3 from such a calculation. According to our results (see below) for both SiO_2 and Al_2O_3, the surface S_{12} differs significantly between the two-phase and three-phase systems, perhaps due to the effect of treatment of the support during catalyst preparation.

The uncorrelated Voronoi cell model, as seen in Eq. (2), expresses all the P_{ij} in terms of volume fractions and $p_0(r)$, which is $\gamma(r)$. Thus, the surfaces are given by

$$S_{ij}/V = 4P'_{ij}(0) = -4\phi_i\phi_j p'_0(0) \quad (23)$$

and $p'_0(0) = \gamma'(0) = -1.57724/l$. The results for the surfaces of Pt/SiO_2 and Pt/Al_2O_3 are given in Table 3, using $\gamma'(0)$ calculated from the Voronoi fits. The correlated-cell model gives S_{ij}/V in terms of the ψ_{ji}, as given in Eq. (16). However, only the weighted sum, Eq. (13), is available from experiment, not the individual ψ_{ij}. An additional assumption is necessary.

Suppose we assume the same intercell correlation for all phases, i.e., that ψ_{ij}/ϕ_i is the same for all i and j. Note that this assumption is consistent with (3). Denoting the ratio ψ_{ij}/ϕ_i by X, we find from (13)

$$D = 1 - X$$

($X = 1$ corresponds to no correlation). The surface areas are then given by

$$\begin{aligned} S_{ij}/4V &= X\phi_j\phi_i p'_1(0) \\ &= (1 - D)\phi_j\phi_i(1.57724/l). \quad (24) \end{aligned}$$

Results are in Table 3, using the l values obtained by fitting to the correlated-cell model.

The parameter D may be expressed in terms of the surface areas. Using (16) and (13), we write

$$D = 1 - 0.1585 l V^{-1} \sum_{ij} S_{ij}(n_i - n_j)^2 \Big/ \sum_{ij} \phi_i\phi_j(n_i - n_j)^2.$$

Setting this equal to 0.0952 in the case of Pt/SiO_2, with $l = 86.73$, we have

$$0.0658 \text{ Å}^{-1} = (6.030S_{12} + 282.66S_{13} + 371.26S_{23})/V. \quad (25)$$

We may expect S_{13} and S_{23} to be several orders of magnitude smaller than S_{12} but the larger weights on S_{13} and S_{23} mean their complete neglect is unjustified. However, it is reasonable to approximate their values by what we obtain from uncorrelated cells, i.e., 4.2×10^{-6} and 19.7×10^{-6}. Then we obtain $S_{12}/V = 0.00950$ Å^{-1}, identical to the results from uncorrelated cells or from Eq. (24). The surface of unmetallized SiO_2 was 0.01006 Å^{-1} from (17) and (18). For Pt/Al_2O_3, we have instead of (25)

$$0.0691 \text{ Å}^{-1} = (5.923S_{12} + 82.31S_{13} + 132.39S_{23})/V.$$

Approximating S_{13} and S_{23} by the values from the uncorrelated-cell model, we find $S_{12}/V = 0.00977$ Å^{-1}, which is close to the value found from Eq. (24). The surface for Al_2O_3 was 0.00923 Å^{-1}, from (17) and (18).

Thus, the correlated-cell model, applied to these systems, can yield the support-void surface S_{12} to a few percent, since it is insensitive to the assumptions made for the metal surfaces. The values for the metal surface should be correct to 1–2 significant figures, judging by the agreement between the results of Table 2.

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