Voronoi Cells: An Interesting and Potentially Useful Cell Model for Interpreting the Small-Angle Scattering of Catalysts

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Dedicated to Professor O. Kratky on his 80th birthday

Abstract

A structural model, based on Voronoi polyhedral cells partly filled with support and metallic catalyst, is proposed for interpreting the small-angle X-ray scattering of heterogeneous catalysts. The model's properties are described, and the model is applied to porous Al₂O₃ and Pt/porous Al₂O₃. Surface areas calculated from the X-ray data by means of the statistical geometry of Voronoi tessellations are found in good agreement with those determined by BET (Brunauer, Emmett & Teller) adsorption methods.

Introduction

Various models have been used to interpret the intense small-angle X-ray scattering (SAXS) observed for heterogeneous catalysts such as porous oxides (Al₂O₃, SiO₂, etc.) and oxide-supported metals (Pt/Al₂O₃, Rh/SiO₂, etc.) (Debye, Anderson & Brumberger, 1957; Goodisman & Brumberger, 1971; Whyte, Kirklin, Gould & Heinemann, 1972; Renouprez & Imelik, 1973; Renouprez, Hoang-Van & Compagnon, 1974; Goodisman, Brumberger & Cupelo, 1981). These models generally yield certain characteristic parameters such as surface-to-volume ratios, measures of the average size of the electron density inhomogeneities, and, if a distribution function is known or assumed, size distributions. Several models in which the sample volume is subdivided into cells (either of uniform or variable size) which are then filled according to some prescription with the phases (void, support, metal, each considered to possess an internally uniform electron density) have recently been proposed (Goodisman & Coppa, 1981; Coppa & Goodisman, 1981). The cells may or may not form a regular lattice. The simplest such models postulate uncorrelated cells, filled randomly so that the probability that a particular cell contains material of a given phase is the volume fraction of that phase in the sample. The properties of these models are intrinsically interesting and related to various aspects of geometric probability and percolation theory (Shantz & Kirkpatrick, 1971; Powell, 1979).

A cell model based on the geometry of Voronoi polyhedra (also called Dirichlet regions or tessellations) was applied to the study of liquid structure by Bernal and others (Bernal & Finney, 1967; Finney, 1970), and recently to microemulsions (Kaler & Prager, 1982). These irregular polyhedral cells afford a more realistic description of the catalyst structure than regular lattice models, and some of the required statistical-geometric relationships are known (see, for instance, Meijering, 1953). They offer some other advantages which will be described below.

Scattering theory

We proceed from the general relationships for the SAXS of spatially isotropic systems (Brumberger, 1968). The scattered intensity I(h) (where h = 4πλ⁻¹ × sin θ, λ is the X-ray wavelength, θ is half the scattering angle) is expressed in terms of the correlation function γ(r). The electron density of the ith phase is nᵢ, the corresponding volume fraction qᵢ, n is the average electron density of the sample, and ηᵢ is the electron density fluctuation within phase i from the average value: ηᵢ = nᵢ - n. If x designates some location in the sample, then

\[ γ(r) = \frac{\eta(x)\eta(x + r)}{\eta^2}. \]  

The averaging is over all positions x and all orientations of r in the sample; ηᵢ is the mean-square electron density fluctuation. In terms of γ(r),

\[ I(h) = I_0(h)V\eta^2 \int_0^\infty 4πr^2γ(r)\sin\frac{hr}{\eta^2} dr. \]  

V is the illuminated sample volume, and

\[ I_0(h) = I_0\left(\frac{e^2}{mc^2}\right)^2 \frac{1 + \cos^2 2θ}{2l^2}. \]

I₀ is the incident intensity, \((e^2/mc^2)^2\) the Thomson
cross section of the electron for X-ray scattering, \( l \) the sample–detector distance; for small scattering angles, \( I_\varepsilon(h) \) is effectively constant for constant source intensity. The problem reduces to the calculation of \( \gamma(r) \), and its Fourier transformation. For a system of \( N \) phases, each of uniform density, \( \gamma(r) \) can be expressed in terms of the probabilities \( P_{ij}(r) \) that a line segment of length \( r \) will have one end in phase \( i \) and the other simultaneously in phase \( j \) (Goodisman & Brumberger, 1971):

\[
\gamma(r) = \frac{\sum_{i,j=1}^{N} P_{ij}(r)n_i n_j - n^2}{n^2 - n^2}. \tag{4}
\]

For uncorrelated cells, this reduces further, independently of cell shape, to \( P_0(r) \), the probability that \( r \) lies wholly within one cell ('non-crossing probability') (Goodisman & Coppa, 1981). For multi-cell-size models, \( \gamma(r) \) will be a sum of terms, each representing a particular size; for two cell sizes, indicated by superscripts (1) and (2),

\[
\gamma(r) = (1 - A)P_0^{(1)} + AP_0^{(2)}. \tag{5}
\]

For \( N = 3 \) (metallic catalyst, support, voids), there are several alternative ways of filling the cells. We may, for example, fill a volume fraction \( \varphi_1 \) with support. The remaining volume fraction \( 1 - \varphi_1 \) is then subdivided into the smaller cells (if two sizes are employed), which are in turn filled partly with metal and left partly void, according to the volume fractions of these phases (\( \varphi_2 \) for voids, \( \varphi_3 \) for metal, say). We then find (Coppa, 1980; Coppa & Goodisman, 1981)

\[
\gamma(r) = P_0^{(1)} + \frac{(P_0^{(2)} - P_0^{(1)})(n_2 - n_3)^2 \varphi_2 \varphi_3}{(n^2 - n^2)(1 - \varphi_1)}. \tag{6}
\]

The two-cell-size model may be applied to a two-phase system (support, void). Equation (6) reduces to

\[
\gamma(r) = P_0^{(1)} \left[ 1 - \frac{\varphi_3}{\varphi_4} - \frac{\varphi_3}{\varphi_1(1 - \varphi_1 + \varphi_3)} \right] + P_0^{(2)} \left[ \frac{\varphi_3}{\varphi_4(1 - \varphi_1 + \varphi_3)} \right], \tag{7}
\]

when \( n_3 \) is set equal to \( n_1 \), and \( \varphi_4 \), the total volume fraction of support, is made equal to \( \varphi_1 + \varphi_3 \). \( \varphi_3 \) now becomes a parameter of the model, determined from the ratio of the coefficients of \( P_0^{(1)} \) and \( P_0^{(2)} \) in (7) which is found by fitting \( \gamma(r) \) to the experimental data. \( P_0^{(1)} \) refers to the large cells, \( P_0^{(2)} \) to the small ones. If we set \( n_3 = n_2 \), this results in a model with large cells only. The correlation function reduces to a single non-crossing function; we have found that such a model does not represent the observations well.

The scheme we used for three phases is somewhat different from that described by (6), and leads to better agreement with experimental results. It involves going from a four-phase to a three-phase system by a procedure analogous to the development of (7) from (6). The correlation function for the four-phase system is found from (4). A volume fraction \( \varphi_1 \) of the large cells is filled with support; the large cells in the remaining volume fraction, \( 1 - \varphi_1 \), are then each subdivided into small cells, which are filled with phases 2, 3 and 4 according to the appropriate volume fractions. If we let \( f_2, f_3 \) and \( f_4 \) be the volume fractions of phases 2, 3 and 4 in the volume fraction \( 1 - \varphi_1 \), only, we have

\[
f_2 + f_3 + f_4 = 1 \tag{8}
\]

and

\[
\varphi_2 = f_2(1 - \varphi_1),
\varphi_3 = f_3(1 - \varphi_1),
\varphi_4 = f_4(1 - \varphi_1) \tag{9}
\]

so that

\[
\frac{\varphi_2}{\varphi_3} = \frac{f_2}{f_3}. \tag{10}
\]

The correlation function becomes

\[
\gamma(r) = P_0^{(1)} + [P_0^{(2)} - P_0^{(1)}](1 - \varphi_1)[f_2 f_3 (n_2 - n_3)^2
+ f_2 f_4 (n_2 - n_4)^2 + f_3 f_4 (n_3 - n_4)^2] \times (n^2 - n^2)^{-1}. \tag{11}
\]

Letting \( n_4 = n_1 \), \( \varphi_4 = \varphi_1 + \varphi_4 \) we reduce the system to three phases, with support filling a volume fraction \( \varphi_1 \) of large cells and an additional fraction \( f_4 \) of the small ones, and with metal or void phases found in small cells only. The filling is done randomly.

To apply these equations to experimental scattering data, we choose the three independent parameters in \( \gamma(r) \) as given by (5) – the two size parameters in \( P_0^{(1)} \) and \( P_0^{(2)} \), and \( A \) – and its transform to give the best non-linear least-squares fit to the experimental intensity \( I(h) \) (Goodisman & Coppa, 1981; Coppa & Goodisman, 1981). The non-crossing function \( P_0 \) is calculated conveniently for the chosen cell shape in terms of a single scaling parameter, to accommodate different sizes. The volume fractions \( \varphi_1, \varphi_2, \varphi_3 \) and \( \varphi_4 \) are known for the three-phase systems (from bulk and skeletal density determinations and the known densities of the three phases). Similarly, \( \varphi_2 \) and \( \varphi_3 \) are known for the two-phase materials. For \( N = 3 \), we have the relationships of (8)–(10) and the ratio of coefficients of \( P_0^{(1)} \) and \( P_0^{(2)} \) in (11). Consequently, \( \varphi_1, \varphi_2, \varphi_3 \) can be determined. For \( N = 2 \), \( \varphi_3 \) can be determined from the ratio of coefficients in (7). From these quantities and the two length parameters for the large and small cells, the surface-to-volume ratios can be found, as we show in the following sections.
Voronoi cells

The Voronoi cells are determined, starting from a random spatial distribution of defining points of average density \( c \), by bisecting with planes the lines joining each pair of points, and taking the closest planes about each point. Every part of a Voronoi cell is then closer to its defining point or nucleus than to any other defining point. Such a cell is shown, for two dimensions, in Fig. 1. The geometry of the system is determined if the average density of the randomly distributed polyhedral nuclei or 'Poisson points' is given. The probability that two points, separated by a distance \( r \), lie in the same cell is given by (Kaler & Prager, 1982)

\[
\gamma(r) = P_0(r) = c \int_0^\infty \exp \left[ -c \psi(r,s,\alpha) \right] d^3s. \tag{12}
\]

The volume \( \psi \) is that contained within a sphere of radius \( |s| \) centered at \( x \) and a sphere of radius \( |s+r| \) centered at \( x+r \), counting the overlap only once. To obtain (12), we first calculate the probability that: (1) the nearest Poisson point to \( P(x) \) is a distance \( |s| \) away, i.e. there are no Poisson points in a sphere of radius \( s = |s| \) centered on \( P(x) \), but there is one in the sphere of radius \( s + ds \); (2) given (1), the Voronoi cell containing \( P(x+r) \) is the same as that containing \( P(x) \), i.e. there are no Poisson points in the sphere of radius \( |s+r| \) centered on \( P(x+r) \); (3) the angle between \( s \) and \( r \) is \( \alpha \). The product of the three probabilities is (with \( V' \) the volume of the large sphere minus that of the small one)

\[
\exp \left[ -c(4\pi s^3/3) \right] \times 4\pi s^2 c \times \exp \left[ -c V' \right] \times \frac{1}{2} \sin \alpha \, d\alpha
\]

\[= 2\pi c \exp \left[ -c \psi(r,s,\alpha) \right] s^2 ds \sin \alpha \, d\alpha.
\]

Integrating over all \( s \) and \( \alpha \) we obtain (12). The volume \( \psi \) may be written

\[
\psi = \pi \left( \frac{2s^3}{3} + \frac{2r^3}{3} + rs^2 + 2r^2s \cos \alpha \right)
\]

\[\tag{13}
+ \frac{2R^3}{3} + r^2s^2 \cos^2 \alpha
\]

Fig. 1. Construction of Voronoi polygon.

with

\[
R^2 = r^2 + s^2 + 2rs \cos \alpha.
\]

In terms of the bipolar coordinates \( \mu = r^{-1}(s + R) \) and \( \nu = r^{-1}(s - R) \),

\[
\psi' = \pi r^3 \left( \frac{\mu^3}{6} + \frac{\nu^2}{2} - \frac{1}{12} + \frac{(\mu - \nu)^2}{4} + \frac{\mu^2\nu^2}{4} \right). \tag{14}
\]

Then the integral of (12) becomes

\[
\gamma(r) = 2\pi \int_1^\infty \int_0^1 \nu \left( \frac{1}{3} \nu^2 - \frac{1}{3} + \frac{2\mu^3}{3} \right)
\]

\[+ 2\mu^2 + \mu^2 \nu^2 \right) \, d\nu \, d\mu \tag{15}
\]

where the scaling parameter \( \kappa \) is \( \pi r^3 c/4 \). The calculation of \( \gamma(r) \) is discussed in the Appendix.

For a two-cell-size model, which we have found appropriate to describe the experimentally observed scattering of various catalysts, two average densities \( c_1 \) and \( c_2 \) are used, and the corresponding characteristic lengths and non-crossing probabilities are \( c_1^{-1/3}, c_2^{-1/3}, P_0^{(1)} \) and \( P_0^{(2)} \).

The non-crossing function of the cells is obtained numerically from (15) in terms of \( \pi r^3 c/4 \). The correlation function using a two-cell-size model is then found from

\[
\gamma(r) = (1 - A)P_0(c_1) + AP_0(c_2) \tag{16}
\]

by Fourier transforming (16) numerically to \( I(h) \), and determining the values of \( A, c_1 \) and \( c_2 \) which give the best fit to the experimental \( I(h) \) values. Since \( c_1 \) and \( c_2 \) are average densities, there are now two distributions of polyhedral volumes about the average volumes \( c_1^{-1} \) and \( c_2^{-1} \). In the filling of some of the large cells with small ones, the latter, being irregular, may not fill exactly, and we have neglected such edge effects in our calculations. A somewhat unrealistic feature of the model is that there will be some solid regions surrounded by void; however, rough calculations show that the probability of such occurrences is small.

Surface-to-volume ratios

To calculate surface-to-volume ratios, we multiply the average interfacial area per unit volume, \( 2.91 \, c^{1/3} \) (Meijering, 1953) by the probabilities that the two sides of the interface are filled by the desired two phases. These are combinations of the fractions of space filled by Voronoi cells of the appropriate type (average densities \( c_1 \) and \( c_2 \)) multiplied by appropriate volume fractions.
For the case $N=2$ (support, phase 1 and void, phase 2), there is only one surface-to-volume ratio, $S_{12}/V$. Contributions are made to this by interfaces between large cells filled with support and small void cells, between small support-filled cells and small void cells within the same divided large cell, and between small support-filled and small void cells in different divided large cells. Then

$$S_{12} = 2.91 \left[ c_{1}^{1/3} 2 \varphi_1 (1 - \varphi_1) f_2 ight]$$
$$+ c_{1}^{1/3} 2 (1 - \varphi_1)^2 f_2 (1 - f_2)$$
$$+ (c_{1}^{1/3} - c_{2}^{1/3}) 2 (1 - \varphi_1) f_2 (1 - f_2),$$

(17)

where $f_2$ is the void fraction of small cells, and the factor of 2 is introduced to account for the two mutually exclusive ways each type of interface can be achieved; $f_2 = \varphi_2 / (1 - \varphi_1 + \varphi_3)$.

For $N=3$ (phase 3 = metal), using the model described in (8)-(11), the following relationships for the three possible interfaces are found:

$$S_{12} = 2.91 \left[ c_{1}^{1/3} 2 \varphi_1 (1 - \varphi_1) f_2 + c_{1}^{1/3} 2 (1 - \varphi_1)^2 f_2 f_3 f_4 ight]$$
$$+ (c_{1}^{1/3} - c_{2}^{1/3}) 2 (1 - \varphi_1) f_2 f_4,$$

(18)

$$S_{12} = 2.91 \left[ c_{1}^{1/3} 2 \varphi_1 (1 - \varphi_1) f_3 + c_{1}^{1/3} 2 (1 - \varphi_1)^2 f_3 f_4 ight]$$
$$+ (c_{1}^{1/3} - c_{2}^{1/3}) 2 (1 - \varphi_1) f_3 f_4,$$

(19)

$$S_{23} = 2.91 \left[ c_{1}^{1/3} 2 (1 - \varphi_1)^2 f_2 f_3 ight]$$
$$+ (c_{1}^{1/3} - c_{2}^{1/3}) 2 (1 - \varphi_1) f_2 f_3,$$

(20)

Experimental application

The small-angle scattering of porous Al$_2$O$_3$ and Pt/porous Al$_2$O$_3$ catalysts was measured with Ni-filtered Cu Kα radiation, using a Kratky camera in the 'infinite slit' geometry (Kratky, 1967).† Intensity data, after subtraction of transmission-corrected background scattering, were desmeared (Heine & Roppert, 1962; Brumberger & Kent, 1964). Fig. 2 shows typical second-moment plots of intensity for a porous alumina and a Pt/porous alumina, together with the fitted curves. The values of $A$, $c_{1}^{1/3}$ and $c_{2}^{1/3}$ are listed in Table 1, together with the other data for these samples. Surface-to-volume ratios were calculated from (17)-(20) and converted to specific surface $S^*$:

$$S^* = \frac{S 10^4}{V d_B},$$

(21)

d$_B$ is the bulk density.

The agreement with areas determined by gas adsorption is good, even for the Pt/Al$_2$O$_3$ catalysts, for which the fit to the experimental data is generally not as good as for the porous alumina samples.‡ For two-phase systems, $S/V$ can be determined without special models, if the second moment of the intensity $Q = \int h^2 I(h) dh$ and the constant $k = \lim_{h \to 0} h^4 I(h)$ are known (Brumberger, 1968). It is, however, not uncommon that intensity measurements do not reach sufficiently small angles for the $h^2 I(h)$ vs $h$ curves to pass through their maxima before descending to zero. The extrapolation to $h = 0$ is then extremely uncertain. As the figure shows, these curves, for the catalysts we described here as well as others we have examined, display at least two maxima. The fitted curves from the Voronoi model are based on the entire range of scattering data for each sample and may be extended to the origin. Note that parameters in $\gamma(r)$ are determined by minimizing the mean-square relative deviation between experimental intensities and calculated values for the corresponding scattering angles; no extrapolation is required. The agreement with BET areas indicates that this is a reasonable model for describing the catalyst structure. It should be added that cubic and spherical multi-cell-size models gave significantly poorer fits to the experimental data.

Earlier models proposed for interpreting the small-angle data required the measurement of scattering for metal-free support in addition to that of the catalyst (see, for example, Goodisman, Brumberger & Cupelo, 1968),

†Some limited hydrogen chemisorption data for the Pt/Al$_2$O$_3$ samples indicate $S_2^*$ values comparable to those quoted in Table 1.
Table 1. Comparison of surface areas obtained from Voronoi model scattering and by adsorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
<th>(1 - A)/A</th>
<th>(c_1^{1/3}) (Å)</th>
<th>(c_2^{1/3}) (Å)</th>
<th>(S_{12})</th>
<th>(S_{13})</th>
<th>(S_{23})</th>
<th>Specific surface area (\text{m}^2\text{g}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Porous (\text{Al}_2\text{O}_3)</td>
<td>0.0243</td>
<td>583</td>
<td>42.0</td>
<td>272</td>
<td>-</td>
<td>-</td>
<td>320</td>
</tr>
<tr>
<td>2</td>
<td>Porous (\text{Al}_2\text{O}_3)</td>
<td>0.0267</td>
<td>667</td>
<td>59.1</td>
<td>218</td>
<td>-</td>
<td>-</td>
<td>229</td>
</tr>
<tr>
<td>3</td>
<td>(~4) wt% Pt/porous (\text{Al}_2\text{O}_3)</td>
<td>0.2225</td>
<td>340</td>
<td>43.9</td>
<td>250</td>
<td>0.44</td>
<td>2.20</td>
<td>216</td>
</tr>
<tr>
<td>4</td>
<td>(~7) wt% Pt/porous (\text{Al}_2\text{O}_3)</td>
<td>0.1970</td>
<td>251</td>
<td>43.7</td>
<td>242</td>
<td>0.76</td>
<td>3.91</td>
<td>223</td>
</tr>
<tr>
<td>5</td>
<td>(~11) wt% Pt/porous (\text{Al}_2\text{O}_3)</td>
<td>0.2154</td>
<td>362</td>
<td>51.1</td>
<td>185</td>
<td>0.88</td>
<td>5.11</td>
<td>212</td>
</tr>
</tbody>
</table>

†By \(\text{N}_2\) adsorption. ‡Subscripts denote: 1 support; 2 void; 3 metal.

The procedure proposed here yields all the surface areas from a single measurement. It is therefore not subject to the additional errors introduced by a differential method, nor does it require the assumption that support structure is unchanged by addition of the metal.

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APPENDIX

Evaluation of the non-crossing function

Evaluation of the non-crossing function for all \(r \text{ and } c\) reduces, according to (15), to the evaluation of

\[
F(\kappa) = \int_0^\infty \int_0^1 d\mu \int_0^{\mu^2} dv \left( \mu^2 - v^2 \right) \exp \left[ -\kappa \left( v^2 - \frac{1}{3} + \frac{2\mu^3}{3} \right) + 2\mu v^2 + \mu^2 + \mu^2 v^2 \right]
\]

as a function of \(\kappa\). For small \(\kappa\), we substitute the new variable of integration \(u = \kappa^{1/3}(\mu - 1)\) for \(\mu\), write the integrand as a power series in \(\kappa^{1/3}\), and integrate over \(v\), as follows:

\[
\gamma = 2\kappa^{2/3} \int_0^\infty du \int_0^1 dv \left( \kappa^{-2/3} u^2 + 2\kappa^{-1/3} u + 1 - v^2 \right) \exp \left[ -\kappa \left( \frac{4}{3} + 4v^2 + \frac{2u^3}{3\kappa} + \frac{3u^2}{\kappa^{2/3}} + \frac{4u}{\kappa^{1/3}} \right) + \frac{4uv^2}{\kappa^{1/3}} + \frac{u^2 v^2}{\kappa^{2/3}} \right]
\]

\[
\gamma = \int_0^\infty du \left[ \left( 2u^2 + \kappa^{1/3} \left( 4u - \frac{20u^4}{3} \right) + \kappa^{2/3} \left( \frac{4}{3} - 24u^3 + \frac{56u^6}{5} \right) + \ldots \right) \exp \left( -\frac{2}{3} u^3 \right) \right]
\]

The integrals over \(u\) may either be done exactly or expressed in terms of \(\Gamma\) functions of order 1/3 and 2/3, and we obtain

\[
\gamma = 1 - \frac{8}{9} \kappa^{1/3} \left( \frac{2}{3} \right)^{2/3} \Gamma \left( \frac{2}{3} \right) + \frac{8}{45} \kappa^{2/3} \left( \frac{2}{3} \right)^{1/3} \Gamma \left( \frac{1}{3} \right) + \ldots
\]

A large-\(\kappa\) form for \(\gamma\) may be obtained by making the substitution \(u = \mu - 1\) in (A1) and extending the integration over \(v\) to the range from \(-\infty\) to \(+\infty\), obtaining

\[
\gamma = \kappa \int_{-\infty}^{+\infty} dv \exp \left[ -\kappa \left( \frac{4}{3} + 4v^2 \right) \right] \times \int_0^\infty du \left( u^2 + 2u + 1 - v^2 \right) \exp \left[ -\kappa \left( \frac{2}{3} u^3 + 3u^2 + 4u + 4uv^2 + u^2 v^2 \right) \right].
\]

The change in the limits of integration is equivalent to neglecting terms in \(\exp(-4\kappa)\) compared to unity. The integration over \(v\) may now be carried out to give

\[
\gamma = \kappa \exp \left( -\frac{4}{3} \kappa \pi/\kappa^2 \right) \int_0^\infty du \left[ \frac{(u + 1)^2}{u + 2} - \frac{1}{2\kappa(u + 2)^3} \right] \exp \left[ -\kappa \left( \frac{2}{3} u^3 + 3u^2 + 4u \right) \right].
\]
Successive integrations by parts will now give a series in $\kappa^{-1}$, i.e.

$$\gamma = \frac{1}{8} \exp\left( -\frac{4}{3} \kappa \right) \left( \frac{\pi}{\kappa} \right)^2 \left( 1 - \frac{1}{8\kappa} + \frac{1}{16\kappa^2} \ldots \right). \quad (A6)$$

The above expression is accurate to 1% for $\kappa > 2$. For intermediate values of $\kappa$, we evaluate $\gamma$ numerically by crossed Gaussian quadratures over $v$ and $\mu$.

Note added in proof: It should be pointed out that the alternative physically reasonable choice of void for phase 1 leads to somewhat different but similar surface areas $S^*_3$ for the three-phase case. For two phases, areas are invariant to an interchange of phases.

References