Leading asymptotic term of the small-angle scattered intensity

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It is shown that the leading asymptotic term of the small-angle intensity scattered by any amorphous sample is determined by the parallelism among subsets of the sample interfaces. Its general expression is $\sum_l[\mathcal{A}_l\cos(\delta_l h)+\mathcal{B}_l\sin(\delta_l h)]/h^4$, where the δ_l's denote the distances between parallel surfaces and the $\mathcal{A}_l$'s and the $\mathcal{B}_l$'s are appropriate geometrical averages of the corresponding Gaussian curvatures. Since each surface is parallel to itself with a relative null distance, in the former expression the well-known Porod contribution comes out from the term relevant to $\delta=0$. The expression is specialized to the case of those three-component samples where one of the constituting phases has a constant thickness and lies in between the remaining two phases which have no common interface. Different approximations are considered and, in the most favorable cases, it appears that the average Gaussian, mean, and squared mean curvatures of the dividing film can be determined.

I. INTRODUCTION

The main assumption [1] of small-angle scattering (SAS) theory is that $n(\mathbf{r})$, the electron or the scattering-length density of the sample depending on the nature of the incident beam, can be approximated by a discrete valued function $n_D(\mathbf{r})$, i.e., by a function that assumes only a finite number of values: $n_1, n_2, \ldots, n_N$. In this way, the sample is idealized as made up of N different homogeneous phases and it is fully characterized once the densities n_i and the regions $\mathcal{V}_i$, occupied by the constituting phases, are known. In other words, by the aforesaid idealization, referred to later as Debye's idealization [1,2], one neglects all density fluctuations internal to the $\mathcal{V}_i$'s. Clearly the approximation will surely fail when one looks at the internal sample structure with a high resolution, i.e., at large momentum-transfer ($\equiv h$) values. On the one hand, the geometrical features of the interphase surfaces, i.e., the boundaries $\mathcal{S}_i$ of the $\mathcal{V}_i$'s, affect mainly the asymptotic behavior of the so-called standard scattered intensity [3] $I(h)$. On the other hand, it is possible that the onset of the asymptotic behavior takes place at h values sufficiently small for Debye's idealization to be still accurate, as it has recently been found in some cases [4]. Therefore, a better knowledge of the relation existing between the interface shapes and the asymptotic expansion of the scattered intensity is not useless, also from a practical point of view. In this paper we shall focus our attention on the *leading* asymptotic term [$\equiv I_{\mathrm{LAT}}(h)$]. In fact, we shall show that its more general expression is

$$I_{\mathrm{LAT}}(h)=\sum_{l=1}^{M}\frac{\mathcal{A}_l\cos(\delta_l h)+\mathcal{B}_l\sin(\delta_l h)}{h^4}\ . \tag{1.1}$$

Before knowing the meaning of the symbols present in (1.1), one wonders where all these contributions come out and where the well-known Porod contribution [5,6] has finished. Indeed, we shall show that the appearance of these contributions is related to a particular geometrical property that interfaces may have: namely, the *parallelism* property. Let us first recall the latter's definition and some of its consequences. Two surfaces Σ_1 and Σ_2 are said to be parallel when each straight line orthogonal to one surface is also orthogonal to the other. This definition generalizes the one well known between planar surfaces and it implies that the distance ($\equiv\delta$), evaluated along the normal lines, is the same at each point of the surfaces. Moreover, one should note that a surface is always parallel to itself with a relative null distance, e.g., $\delta=0$, while, in some cases, it can also turn out parallel to itself with a different distance value. For instance, a sphere of radius R is parallel to itself both with $\delta=0$ and $2R$.

We now come back to Eq. (1.1) and define the quantities involved there. Clearly, $\delta_1,\delta_2,\ldots,\delta_M$ denote the distances where the parallelism occurs. (We consider M finite for simplicity.) The $\mathcal{A}_l$'s and the $\mathcal{B}_l$'s are given by appropriate integral expressions over the corresponding parallel interfaces subsets [see Eqs. (3.17) and (3.18) and (3.13 and (3.14)]. Moreover, the $\mathcal{A}_l$ expression, when $\delta_l=0$, reduces to the well-known Porod expression. Since any surface is parallel to itself at a relative null distance, then one of the δ_l's will certainly be equal to zero. Thus, choosing $\delta_1=0$, we can say that the first term of the sum on the right-hand side (rhs) of (1.1) yields the Porod contribution. Each of the remaining contributions, characterized by $\delta_l\neq 0$, shows an oscillatory (damped) behavior and for this reason their sum will be referred to as the *oscillatory* deviation from the Porod law. Moreover, the presence of oscillations proportional either to the cosine or to the sine functions is not new. Indeed, deviations proportional to the cosine have been noted in the asymptotic expansion of the form factors of spherical [7] and of prismatic particles [8], while a deviation proportional to the sine function has first been found by Schmidt [9] in the case of right circular cylinders. More recently [10], these results have been generalized and put into a form close to that of Eq. (1.1). In the present paper we

make the proof complete showing that deviations different from the sine and the cosine ones do not exist when interphase boundaries are assumed almost everywhere smooth. Besides, we shall considerably simplify the expressions of coefficients $\mathcal{A}_l$ and $\mathcal{B}_l$ and we shall illustrate how Eq. (1.1) can find useful applications in analyzing the intensities scattered by the samples where one of the constituting phases has a constant thickness.

The plan of the paper is the following. In Sec. II, we report the general main formulas of SAS theory. In Sec. III we discuss some properties of parallel surfaces and particularly the relation existing between their curvature radii at *correspondent* points (for this definition see the end of Sec. III A). This relation, in turn, allows us to prove that deviations, different from the ones reported in (1.1), do not exist as well as to simplify the $\mathcal{A}_l$ and $\mathcal{B}_l$ expressions. In Sec. IV the result is applied to the samples just mentioned, while Sec. V contains some conclusive remarks.

II. CORRELATION FUNCTION PROPERTIES

A. Definitions and assumptions

For isotropic samples, the standard [3,2] scattered intensity is given by

$$I(h)=\frac{4\pi V\langle\eta^2\rangle}{h}\int_0^\infty r\gamma(r)\sin(hr)dr \ , \tag{2.1}$$

where $\gamma(r)$, the isotropic component of the autocorrelation function [1] of the sample, is defined as

$$\gamma(r)\equiv(4\pi V\langle\eta^2\rangle)^{-1} \times\int d\hat{\omega}\int_{R^3}\eta(\mathbf{r}_1+r\hat{\omega})\eta(\mathbf{r}_1)dv_1 \ , \tag{2.2}$$

and $\eta(\mathbf{r})\equiv[n(\mathbf{r})-\langle n\rangle]$ represents the fluctuation of $n(\mathbf{r})$ (the electronic or the scattering-length density of the sample) with respect to its average value $\langle n\rangle$. Moreover, V and $\langle\eta^2\rangle$ denote, respectively, the volume and the mean-squared fluctuation of the sample, while the first integral on the rhs of (2.2) amounts to integrating over all possible directions of the unit vector $\hat{\omega}$. Approximating $n(\mathbf{r})$ by $n_D(\mathbf{r})$, $\eta(\mathbf{r})$ can be written in terms of the so-called characteristic functions $\rho_i(\mathbf{r})$ of the sets $\mathcal{V}_i$ [11]. [We recall that $\rho_i(\mathbf{r})$ is defined as equal to one inside $\mathcal{V}_i$ and to zero outside $\mathcal{V}_i$.] By some algebraic manipulations [12,13], one proves that

$$\gamma(r)=1-\sum_{\substack{i,j=1\\ j>1}}^{N}(n_i-n_j)^2P_{ij}(r)/\langle\eta^2\rangle \tag{2.3}$$

and

$$\langle\eta^2\rangle=\sum_{i=1}^{N}(n_i-\langle n\rangle)^2\phi_i =\sum_{\substack{i,j=1\\ j>i}}^{N}(n_i-n_j)^2\phi_i\phi_j, \quad \phi_i\equiv V_i/V \ ,$$

with

$$P_{ij}(r)\equiv(4\pi V)^{-1}\int d\hat{\omega}\int_{R^3}\rho_i(\mathbf{r}_1)\rho_j(\mathbf{r}_1+r\hat{\omega})dv_1 =(4\pi V)^{-1}\int d\hat{\omega}\int_{\mathcal{V}_i}dv_i\int_{\mathcal{V}_j}dv_j\delta(\mathbf{r}_i+r\hat{\omega}-\mathbf{r}_j) \ . \tag{2.4}$$

[V_i denotes the volume of the ith phase region $\mathcal{V}_i$ and $\delta(\cdots)$ is the Dirac function.] We note that, in obtaining Eq. (2.3), the contribution due to the boundary of the sample has been assumed to be negligible. A convenient way for assuring this condition is to assume an infinite (and nonpathological) volume limit of the sample. More definitely, we shall assume that (a) except for sets having zero measure, the phase boundaries are *smooth* surfaces, (b) the area S_i of the surface $\mathcal{S}_i$, enveloping the ith phase, is such that S_i/V tends to a finite value as $V\to\infty$ [note that assumptions (a) and (b) definitely rule out any fractal behavior], and (c) at large distances, whatever i and j, $P_{ij}(r)-\phi_i\phi_j$ decreases at least as $1/r^{1+\epsilon}$ (with $\epsilon>0$) and that the asymptotic behavior of any $P_{ij}(r)$ derivative we shall later consider is given by the corresponding derivative of the aforesaid asymptotic expression. (Note that the assumed decrease behavior is much weaker than in the exponential case. Roughly speaking, this amounts to saying that our analysis holds true also close to a "critical point.")

By assumptions (a) and (b), and from Eqs. (2.3) and (2.4) it immediately follows that $\gamma(r)$ is a continuous function. Moreover, using the integral expression of $P'_{ij}(r)$ [the first derivative of $P_{ij}(r)$] reported in [11], one shows [10] that $P'_{ij}(r)$ and $\gamma'(r)$ are also continuous.

B. Parallel surfaces and singularities of the second derivative of $\gamma(r)$

By contrast, $P''_{ij}(r)$, the second-order derivative of $P_{ij}(r)$, can be discontinuous at some r values, generally denoted by δ. The geometrical feature of the interphase surfaces responsible for this phenomenon has been isolated [10] starting from the two integral expressions of $P''_{ij}(r)$ obtained in Ref. [11],

$$P''_{ij}(r)=-(4\pi V)^{-1}\int d\hat{\omega}\int_{\mathcal{S}_i}dS_i\int_{\mathcal{S}_j}dS_j[\hat{\sigma}_i(\mathbf{r}_i)\cdot\hat{\omega}][\hat{\sigma}_j(\mathbf{r}_j)\cdot\hat{\omega}]\delta(\mathbf{r}_i+r\hat{\omega}-\mathbf{r}_j) \tag{2.5}$$

or

$$P''_{ij}(r)=-(4\pi Vr^2)^{-1}\int_{\mathcal{S}_i}dS_i\mathcal{L}_j(\mathbf{r}_i,r) \tag{2.6}$$

with

$$\mathcal{L}_j(\mathbf{r}_i,r)\equiv\oint_{\Gamma_j(\mathbf{r}_i,r)}dl[\hat{\sigma}_i(\mathbf{r}_i)\cdot\hat{\omega}(l)]\cot\{\arccos[\hat{\sigma}_j(\mathbf{r}_j)\cdot\hat{\omega}(l)]\} \ . \tag{2.7}$$

Here $\hat{\sigma}_i(\mathbf{r}_i)$ denotes the unit vector pointing externally to the ith phase and orthogonal to the infinitesimal element dS_i (set at the point characterized by the position vector $\mathbf{r}_i$) of surface $\mathcal{S}_i$. [$\hat{\sigma}_j(\mathbf{r}_j)$ is similarly defined. Moreover, we shall often use the simpler notation $\hat{\sigma}_j$, omitting to specify the point coordinates.] The Dirac function requires that the two points, denoted by $\mathbf{r}_i$ and $\mathbf{r}_j$ and lying, respectively, on $\mathcal{S}_i$ and $\mathcal{S}_j$, are far apart r along the direction $\hat{\omega}$. Taking $\mathbf{r}_i$ fixed and letting $\hat{\omega}$ vary over all possible directions, the former constraint will single out the curve, denoted by $\Gamma_j(\mathbf{r}_i,r)$ in Eq. (2.7), resulting from the intersection of $\mathcal{S}_j$ with $\mathcal{S}(\mathbf{r}_i,r)$, the sphere of radius r, and center at $\mathbf{r}_i$. Finally, in Eq. (2.7), $\hat{\omega}(l)$ is the direction of the line going from $\mathbf{r}_i$ to the infinitesimal element dl (characterized by the curvilinear coordinate l and set at the point $\mathbf{r}_j$) of the curve $\Gamma_j(\mathbf{r}_i,r)$. From Eqs. (2.6) and (2.7) it follows that $P_{ij}''(r)$ can be singular only when an $\mathcal{S}_i$ subset is parallel to an $\mathcal{S}_j$ subset. In fact, the integrand of (2.7) is singular when $\hat{\sigma}_j(l)$ and $\hat{\omega}(l)$ are parallel, i.e., $\hat{\sigma}_j=\hat{\omega}$ or $-\hat{\omega}$. Whenever $\hat{\sigma}_i(\mathbf{r}_i)$ were not parallel to the previous vectors, the former singularity would not be really present, since one could locally consider as $P_{ij}''(r)$'s expression the one obtained by interchanging index i with index j in Eq. (2.6). Thus, a singularity of $P_{ij}''(r)$ can exist only when $\hat{\sigma}_i(\mathbf{r}_i)$, $\hat{\sigma}_j(l)$, and $\hat{\omega}(l)$ are parallel and this amounts to saying that the corresponding surface elements dS_i and dS_j are parallel. Of course, for a singularity really to exist, the aforesaid parallelism has to occur for an $\mathcal{S}_i$ subset which has a finite measure. The nature of the singularity depends on the behavior of $\mathcal{L}_j(\mathbf{r}_i,r)$ as r approaches δ, the distance between the present parallel interface subsets.

C. Contact nature and singularity behavior

Although this problem has been thoroughly discussed in Ref. [10], for the sake of completeness we shall recall the main points of that analysis. First of all we note that $\mathcal{S}_j$ and $\mathcal{S}(\mathbf{r}_i,\delta)$ will be tangent at the aforesaid point $\mathbf{r}_j$, denoted by $\mathbf{r}_j(\delta)$ in order to make the underlying parallelism more evident. The behavior of $\mathcal{L}_j(\mathbf{r}_i,r)$, as $r\to\delta$, in general depends on the relative spatial position of $\mathcal{S}_j$ and $\mathcal{S}(\mathbf{r}_i,r)$ in a small neighborhood of $\mathbf{r}_j(\delta)$. Two cases are possible: (a) $\mathcal{S}(\mathbf{r}_i,r)$ intersects $\mathcal{S}_j$ both when $r<\delta$ and when $r>\delta$; (b) $\mathcal{S}(\mathbf{r}_i,r)$ intersects $\mathcal{S}_j$ either when $r<\delta$ or when $r>\delta$. In case (b), $\mathcal{S}(\mathbf{r}_i,r)$ will lie only on one side with respect to $\mathcal{S}_j$ and then, when $r=\delta$, the two surfaces will only share the point $\mathbf{r}_j(\delta)$ [14]. On the contrary, in case (a), the two surfaces will always have a curve in common and the latter will be tangent to both surfaces at $\mathbf{r}_j(\delta)$, when $r=\delta$. Since the integrand of (2.7) diverges as $r\to\delta$, in case (a), at least a logarithmic divergence of $\mathcal{L}_j(\mathbf{r}_i,r)$ in general has to be expected. In case (b), the limit of the integral (2.7) will be zero as $r\to\delta$ from that side where no intersection occurs (say $r\to\delta^-$) and it can be finite as $r\to\delta^+$, since the divergence of the integrand can be cured by the vanishing of the integration domain. Thus, $\mathcal{L}_j(\mathbf{r}_i,r)$ can have a discontinuity at $r=\delta$. Of course, these results hold true, provided the integrand in (2.7) does not diverge too fast. This condition is surely met when the contact between $\mathcal{S}_j$ and $\mathcal{S}(\mathbf{r}_i,\delta)$ is *simple*. In order to formulate this condition and obtain the leading behavior of $\mathcal{L}_j(\mathbf{r}_j,r)$ as $r\to\delta$, we consider a Cartesian frame having the origin at dS_i and as z axis the line joining dS_i with the element of dS_j set at $\mathbf{r}_j(\delta)$. Around this point, let $z=f_j(x,y)$ and $z=f_{\mathcal{S}}(x,y)\equiv\sqrt{\delta^2-x^2-y^2}$ denote the equations of $\mathcal{S}_j$ and of $\mathcal{S}(\mathbf{r}_i,\delta)$, respectively. Let $F_j(x,y)\equiv f_j(x,y)-f_{\mathcal{S}}(x,y)$. The contact is named *simple* when the hessian of F_j, defined as

$$\mathcal{H}_j(\mathbf{r}_i,x,y)\equiv\det\begin{bmatrix}F_{j,xx} & F_{j,xy}\\ F_{j,xy} & F_{j,yy}\end{bmatrix}, \tag{2.8}$$

turns [15] out different from zero at the origin. Otherwise it is of higher order. Thus, the contact between $\mathcal{S}(\mathbf{r}_i,\delta)$ and $\mathcal{S}_j$ is called *elliptic* when it is simple and the two surfaces share only the tangency point, *hyperbolic* when the contact is simple and the two surfaces intersect each other around the tangency point, and, finally, *parabolic* when the contact is not simple, e.g., $\mathcal{H}_j=0$. In the first two cases it has been shown [10] that the singular behavior is given by

$$\mathcal{L}_j(\mathbf{r}_i,\delta^+)-\mathcal{L}_j(\mathbf{r}_i,\delta^-)=2\pi\mathcal{H}_j(\mathbf{r}_i)^{-1/2}[\hat{\sigma}_i(\mathbf{r}_i)\cdot\hat{\sigma}_j(\mathbf{r}_j(\delta))]\mathrm{sgn}(F_{j,xx}+F_{j,yy}), \tag{2.9}$$

$$\mathcal{L}_j(\mathbf{r}_i,r)\approx-2|\mathcal{H}_j(\mathbf{r}_i)|^{-1/2}[\hat{\sigma}_i(\mathbf{r}_i)\cdot\hat{\sigma}_j(\mathbf{r}_j(\delta))]\ln(|r-\delta|)+o \tag{2.10}$$

for the elliptic and the hyperbolic cases [16], respectively. In the parabolic case, in order to isolate the singular behavior, we need to analyze higher-order terms and thus further assumptions are required. In the next section, however, it will be shown that the parabolic contacts take place on sets of null measure so that, in practice, we can ignore their existence.

III. PARALLELISM AND FORM OF THE LEADING ASYMPTOTIC TERM

To this aim, we need to analyze more closely parallel surfaces in order to obtain a relation between the principal curvature radii at *correspondent* points. This relation allows us to get a simple expression for $\mathcal{H}_j(\mathbf{r}_i)$ and to show that the set of points where parabolic contacts take place have a null measure.

A. General recipe for constructing parallel surfaces

Let

$$\mathbf{r}_1=\mathbf{r}_1(u,v) \tag{3.1}$$

denote the parametric equation of a smooth surface Σ_1. The surface Σ_2, defined by the parametric equations

$$\mathbf{r}_2=\mathbf{r}_2(u,v)\equiv\mathbf{r}_1(u,v)+\delta\hat{\boldsymbol{\nu}}_1(u,v)\ , \tag{3.2}$$

is a surface parallel and distant δ from Σ_1. [Here, $\hat{\boldsymbol{\nu}}_1(u,v)$, defined as

$$\hat{\boldsymbol{\nu}}_1(u,v)\equiv\frac{\mathbf{r}_{1,u}(u,v)\times\mathbf{r}_{1,v}(u,v)}{\|\mathbf{r}_{1,u}(u,v)\times\mathbf{r}_{1,v}(u,v)\|}\ , \tag{3.3}$$

is the unit vector orthogonal to Σ_1 at the point $\mathbf{r}_1$ while $\mathbf{r}_{1,u}\equiv\partial\mathbf{r}_1/\partial u$ and $\mathbf{r}_{1,v}\equiv\partial\mathbf{r}_1/\partial v$ are linearly independent vectors parallel to Σ_1.] This statement can be easily proved by showing that $\hat{\boldsymbol{\nu}}_2(u,v)$, the normal to Σ_2 at $\mathbf{r}_2(u,v)$, is parallel to $\hat{\boldsymbol{\nu}}_1(u,v)$.

On the one hand, Eq. (3.2) gives a simple recipe for constructing a surface Σ_2, parallel and far apart δ from a given surface Σ_1. In fact, Σ_2 is the locus of the points described by one end of a stick of length δ, as the opposite end moves throughout Σ_1 and the stick, during its motion, always remains perpendicular to Σ_1. Besides, this construction, or equivalently, Eq. (3.2), defines a natural mapping from Σ_1 to Σ_2 and the points $\mathbf{r}_1(u,v)$ and $\mathbf{r}_2(u,v)$ will be said *correspondent*. On the other hand, using the equations which define the enveloping surface of a family of surfaces [17], it is not difficult to show that Σ_2 is the envelope of the Huyghens wavelets, originating at Σ_1, after these have travelled a distance δ. This property represents, perhaps, a more physical way for defining parallel surfaces: these correspond to different-time configurations of a propagating wave front.

B. Relation between curvature radii

In order to find the above relation, we first recall the definitions of the curvature lines and of the curvature radii of a surface [18,19]. Consider the family of planes, going through the normal to Σ_1 at a point $\mathbf{r}_1$. From the section of each of these planes with Σ_1, one obtains a curve to which one assigns a curvature radius in the following way. One considers the circle osculating the curve and, depending on whether the center lies, or not, in the half-space delimited by the plane tangent to Σ_1 at $\mathbf{r}_1$ and containing $\hat{\boldsymbol{\nu}}_1(u,v)$ (the unit vector orthogonal to Σ_1 at $\mathbf{r}_1$), one assigns, at the considered point of the curve, a curvature radius equal or opposite to the value of the radius of the osculating circle. The principal curvature radii or, more simply, the curvature radii of the surface Σ_1 at $\mathbf{r}_1$ are equal, respectively, to the minimum and to the maximum of the curvature radius values relevant to the curves associated to the aforesaid family of planes. The (principal) curvatures are the reciprocals of the (principal) curvature radii. Finally, the curvature lines are those Σ_1 curves which, at each of their points, have a curvature equal to one of the principal curvatures of Σ_1. By continuity, if a curvature line at one of its points has a curvature equal to the maximum (minimum) of the principal curvature values, then its curvature value will always be equal to the maximum (minimum) principal one. The curvature lines are characterized by the property of meeting each other orthogonally. Moreover, they are uniquely determined by the following property: for a curve Γ_1 lying on Σ_1 to be a curvature line, it is necessary and sufficient that the normals to Σ_1 from each point of Γ_1 have an enveloping curve. By this theorem [18], one easily obtains the relation between the curvature radii of two parallel surfaces Σ_1 and Σ_2. In fact, let us assume that Γ_1 be a curvature line of Σ_1 and let us denote by Γ_2 the curve of Σ_2 obtained from Γ_1 by the mapping (3.2). By the aforesaid theorem, Γ_2 is a curvature line of Σ_2. In fact, the family of normals to Σ_2 through the points of Γ_2 is exactly the one relevant to the curvature line Γ_1 and thus it has an enveloping curve. At this point we use the Rodrigues formula [18] which relates the infinitesimal shift $d\mathbf{r}_1$ along Γ_1, a curvature line of Σ_1, to the variation of the corresponding normal vectors $d\hat{\boldsymbol{\nu}}_1(\mathbf{r}_1)=\hat{\boldsymbol{\nu}}_1(\mathbf{r}_1+d\mathbf{r}_1)-\hat{\boldsymbol{\nu}}_1(\mathbf{r}_1)$ according to

$$d\mathbf{r}_1+R_{1,i}\,d\hat{\boldsymbol{\nu}}_1=0\ ,\quad i=m,M \tag{3.4}$$

where the choice between m and M depends on whether the line has minimal or maximal curvature, respectively. Clearly, one has a similar relation for Γ_2. Recalling that $\hat{\boldsymbol{\nu}}_1$ and $\hat{\boldsymbol{\nu}}_2$ are either equal or opposite, we prefer to write the relation using $\hat{\boldsymbol{\nu}}_1$ instead of $\hat{\boldsymbol{\nu}}_2$ and thus we find

$$d\mathbf{r}_2+R_{2,j}\,d\hat{\boldsymbol{\nu}}_1=0\ ,\quad j=m,M \tag{3.5}$$

where, once again, the choice between $R_{2,m}$ or $R_{2,M}$ will depend on the actual value of the curvature of Γ_2 with reference to the chosen orientation of Σ_2. Differentiating Eq. (3.2), one gets

$$d\mathbf{r}_2=d\mathbf{r}_1+\delta d\hat{\boldsymbol{\nu}}_1\ .$$

Thus, from Eqs. (3.4) and (3.5) it follows that

$$R_{2,j}(u,v)=R_{1,i}(u,v)-\delta\ ,\quad i,j=m,M\ . \tag{3.6}$$

Equation (3.6) represents the sought for relation for the curvature radii. Writing the index values, more explicitly the result corresponds either to

$$\begin{aligned}&R_{2,m}(u,v)=R_{1,m}(u,v)-\delta\ ,\\&R_{2,M}(u,v)=R_{1,M}(u,v)-\delta\end{aligned} \tag{3.7a}$$

or to

$$\begin{aligned}&R_{2,m}(u,v)=R_{1,M}(u,v)-\delta\ ,\\&R_{2,M}(u,v)=R_{1,m}(u,v)-\delta\ .\end{aligned} \tag{3.7b}$$

Initially the choice between (3.7a) and (3.7b) has to be performed by comparing the relevant curvature radii at a pair of correspondent points. Then, the resulting equation will continue to hold true by continuity (as far as one does not meet an umbilical point, a point where the two curvatures are equal, or a singular point).

C. Irrelevance of parabolic contact points

Before discussing this point, we apply the former result in order to simplify the $\mathcal{H}_j(\mathbf{r}_i)$ expression obtained at the end of the previous section. We can identify Σ_1 and Σ_2 with $\mathcal{S}_i$ and $\mathcal{S}_j$ and orient $\mathcal{S}_i$ in such a way that its normal goes from $\mathcal{S}_i$ to $\mathcal{S}_j$. Moreover, we can choose the x and the y axis along the principal directions (e.g., the

tangents to the principal curvature lines) of $\mathcal{S}_i$ at $\mathbf{r}_i$. In this way, the parametric equation of f_j becomes

$$f_j \approx \delta + \frac{1}{2}\left[\frac{x^2}{R_{j,m}} + \frac{y^2}{R_{j,M}}\right] + o$$

in a small neighborhood of the origin. Using the definition of F_j, reported just above Eq. (2.8), and Eq. (3.7a) or (3.7b), one finds

$$\mathcal{H}_j(\mathbf{r}_i) = \frac{R_{i,m}R_{i,M}}{R_{j,m}R_{j,M}\delta^2} \ . \tag{3.8}$$

Recalling that the Gaussian curvature of a surface at a point, where the curvature radii are R_m and R_M, is $\kappa \equiv 1/R_m R_M$, Eq. (3.8) can be put into the more elegant form

$$\mathcal{H}_j(\mathbf{r}_i) = \frac{\kappa_j(\mathbf{r}_j(\delta))\kappa_{\mathcal{S}}}{\kappa_i(\mathbf{r}_i)} \ , \tag{3.9}$$

which involves only the Gaussian curvatures of the three involved surfaces. Equation (3.9) shows that the result does not depend on the chosen frame of reference because the Gaussian curvature is an intrinsic property of the surface [19]. Moreover, it shows that the nature of the contact depends on the curvature values of the parallel surfaces at the correspondent points. In fact, the contact turns out to be elliptic when $\mathcal{S}_i$ and $\mathcal{S}_j$ are both elliptic or both hyperbolic [20] and hyperbolic when one surface is elliptic and the other hyperbolic. The parabolic contact occurs only when

$$R_{1,m} = 0$$

and/or

$$R_{1,M} = 0 \ .$$

However, at a point where one at least of the curvature radii is null or, equivalently, the curvature diverges, the smoothness of the surface fails. Physically these points are real oddities [21]. Therefore, according to assumption (a) of Sec. II A, if these points exist, they form a zero measure set and thus the corresponding divergence of $\mathcal{L}_j(\mathbf{r}_i, r)$ has no consequence because it is washed out by the integration required by Eq. (2.6).

D. $\mathcal{A}_l$ and $\mathcal{B}_l$ expressions

In order to write down the general expression of $P''_{ij}(r)$ around one of its singular points, we shall denote by $\mathcal{S}^E_{i,j}(\delta)$ and $\mathcal{S}^H_{i,j}(\delta)$ the Σ_i subsets which are *elliptically* or *hyperbolically* parallel to (and distant δ from) Σ_j [in the sense that they give rise to elliptic and hyperbolic contacts between $\mathcal{S}(\mathbf{r}_i, \delta)$ and $\mathcal{S}_j$]. Then we substitute Eqs. (2.9) and (2.10) in Eq. (2.6), we use Eq. (3.9), and we find that, around $r = \delta$, the behavior is

$$P''_{ij}(r) \approx -\frac{\Delta^E_{i,j}(\delta)}{2\delta V}\Theta(r-\delta) + \frac{\Delta^H_{i,j}(\delta)}{2\pi\delta V}\ln(|r-\delta|) + c \ , \tag{3.10}$$

where c is a continuous contribution, $\Theta(\ )$ is the Heaviside step function, and

$$\Delta^E_{i,j}(\delta) \equiv \int_{\mathcal{S}^E_{i,j}(\delta)} dS_i \left[\frac{\kappa_i(\mathbf{r}_i)}{\kappa_j(\mathbf{r}_j(\delta))}\right]^{1/2} [\hat{\sigma}_i(\mathbf{r}_i)\cdot\hat{\sigma}_j(\mathbf{r}_j(\delta))]\,\mathrm{sgn}(R_{j,m}R_{i,m'}) \ , \tag{3.11}$$

$$\Delta^H_{i,j}(\delta) \equiv \int_{\mathcal{S}^H_{i,j}(\delta)} dS_i \left[\left|\frac{\kappa_i(\mathbf{r}_i)}{\kappa_j(\mathbf{r}_j(\delta))}\right|\right]^{1/2} [\hat{\sigma}_i(\mathbf{r}_i)\cdot\hat{\sigma}_j(\mathbf{r}_j(\delta))] \ . \tag{3.12}$$

(We recall that $\hat{\sigma}_i$ and $\hat{\sigma}_j$ are, respectively, orthogonal to Σ_i and to Σ_j and point externally to phases i and j. At the denoted points, their scalar product is equal either to 1 or to -1. Since no apparent advantage is gained, we avoid introducing a further decomposition of the integration domains in order to account for this property.) The argument of the sign function in (3.11) deserves an explanatory word. When one uses the frame specified just above Eq. (3.8), the matrix related to the Hessian becomes diagonal at the origin. Since the determinant is positive, the sign of the trace is equal to the sign of one of the matrix elements, which turn out to be equal to $(R_{j,l}+\delta)/(R_{j,l}\delta)$, $l = m, M$. The argument of the sign function reported in (3.11) immediately follows because m' reminds us that we have to choose between (3.7a) and (3.7b) the equation which presently holds true. The symmetry of (3.11) and (3.12), with respect to the exchange $i \leftrightarrow j$, becomes evident if we express the corresponding integrals in terms of the spherical images $\Omega^E_{i,j}(\delta)$ and $\Omega^H_{i,j}(\delta)$ of the two sets $\mathcal{S}^E_{i,j}(\delta)$ and $\mathcal{S}^H_{i,j}(\delta)$ obtained by the Gaussian mapping [19,18] of the latter sets on the unit radius sphere. In fact, using the well-known relation $dS_i = d\hat{\omega}/\kappa_i(\mathbf{r}_i)$ one finds

$$\Delta^E_{i,j}(\delta) = \int_{\Omega^E_{i,j}(\delta)} d\hat{\omega} \frac{\hat{\sigma}_i(\mathbf{r}_i)\cdot\hat{\sigma}_j(\mathbf{r}_j(\delta))}{\sqrt{\kappa_i(\mathbf{r}_i)\kappa_j(\mathbf{r}_j(\delta))}} \times \mathrm{sgn}(R_{j,m}R_{i,m'}) \ , \tag{3.13}$$

$$\Delta^H_{i,j}(\delta) = \int_{\Omega^H_{i,j}(\delta)} d\hat{\omega} \frac{\hat{\sigma}_i(\mathbf{r}_i)\cdot\hat{\sigma}_j(\mathbf{r}_j(\delta))}{\sqrt{|\kappa_i(\mathbf{r}_i)\kappa_j(\mathbf{r}_j(\delta))|}} \ . \tag{3.14}$$

From Eq. (2.3) and the pointed out continuity properties of $P_{ij}(r)$ and of $P'_{ij}(r)$, it follows that $\gamma(r)$ and $\gamma'(r)$ are continuous, while the general behavior of $\gamma''(r)$ around point δ_l is

$$\gamma''(r)\approx\sum_{\substack{i,j=1\\ j>i}}^{M}\frac{(n_i-n_j)^2}{2\delta_l V\langle\eta^2\rangle}\left[\Delta^E_{i,j}(\delta_l)\Theta(r-\delta_l)-\frac{\Delta^H_{i,j}(\delta_l)}{\pi}\ln(|r-\delta_l|)\right]+c\ , \tag{3.15}$$

where c is a contribution continuous around $r=\delta$. In this way the properties and the behavior of $\gamma(r)$ are exactly those discussed in Ref. [10] and thus we can now use the corresponding results in order to obtain the leading asymptotic term of the scattered intensity. In particular, the result that the behaviors given by Eqs. (10a) and (11b) of Ref. [10] give rise to the asymptotic contributions specified by Eqs. (39) and (40) of [10] allows us to conclude that, in general, the leading asymptotic term of the SAS intensity is given by

$$I_{\mathrm{LAT}}(h)=\sum_{l=1}^{M}\frac{\mathcal{A}_l\cos(\delta_l h)+\mathcal{B}_l\sin(\delta_l h)}{h^4} \tag{3.16}$$

with

$$\mathcal{A}_l\equiv-2\pi\sum_{\substack{i,j=1\\ j>i}}^{M}(n_i-n_j)^2\Delta^E_{i,j}(\delta_l)\ , \tag{3.17}$$

$$\mathcal{B}_l\equiv-2\pi\sum_{\substack{i,j=1\\ j>i}}^{M}(n_i-n_j)^2\Delta^H_{i,j}(\delta_l)\ . \tag{3.18}$$

Before concluding this section, we must still show that the well-known Porod contribution

$$2\pi\sum_{\substack{i,j=1\\ j>i}}^{M}(n_i-n_j)^2S_{ij}/h^4$$

is given by the first term of the sum (3.16). Each surface, in fact, is parallel to itself with a relative distance $\delta=0$. Thus (3.16) will always contain at least one term, i.e., the one associated to $\delta=0$. It is convenient to associate this contribution to the index value $l=1$. Our task then is to evaluate $\mathcal{A}_1$. At $\delta=0$, one has that $\mathbf{r}_j(0)=\mathbf{r}_i$, $\hat{\boldsymbol{\sigma}}_i\cdot\hat{\boldsymbol{\sigma}}_j=-1$, the contact throughout the $\mathcal{S}_{ij}$ interface is elliptic, and the remaining factor in the integrand of (3.13) reduces to $d\hat{\omega}/\kappa_i(\mathbf{r}_i)=dS_i$, so that $\Delta^E_{ij}(0)=-S_{ij}$. Substituting in Eq. (3.17), one recovers the Porod result [22].

IV. A GENERAL APPLICATION

We illustrate the relevance of the former analysis to the case of the three-component samples where one phase is a region with constant thickness and separates the remaining two phases. Porous materials with a coating film and oil-water-surfactant systems are the most important practical samples showing the aforesaid feature, since the coating or the surfactant film can be assumed to have a constant thickness to a fair approximation. According to the discussion carried out in Sec. III A, the surfaces delimiting the film are parallel surfaces. Consequently, the asymptotic leading term of the intensity scattered by these samples will certainly contain, besides the Porod term, two contributions proportional to $\cos(\delta h)/h^4$ and to $\sin(\delta h)/h^4$, once we have denoted by δ the thickness of the film. In the following we shall confine ourselves to the case where no further parallelisms are present [23]. In order to specialize Eqs. (3.16)–(3.18) to this case, the densities of the bulk phases will be denoted by n_1 and n_2 and that of the film by n_3. The corresponding interphase surface areas will be $S_{13}\equiv S_1$ and $S_{23}\equiv S_2$, while $S_{12}=0$. Thus, the coefficient of the Porod contribution is

$$\mathcal{A}_0=2\pi[(n_1-n_3)^2S_{13}+(n_2-n_3)^2S_{23}]\ , \tag{4.1}$$

while, from Eq. (3.17), the coefficient of the $\cos(\delta h)/h^4$ contribution will be

$$-2\pi[(n_1-n_2)^2\Delta^E_{12}(\delta)+(n_1-n_3)^2\Delta^E_{13}(\delta)+(n_2-n_3)^2\Delta^E_{23}(\delta)]\ . \tag{4.2}$$

Definition (3.13) implies that the $\Delta^E_{ij}(\delta)$'s, present in (4.2), can differ among themselves only for a sign, related to the relative orientation of the $\hat{\boldsymbol{\sigma}}_i$'s, and then Eq. (4.2) becomes

$$\mathcal{A}(\delta)=2\pi[(n_1-n_2)^2-(n_1-n_3)^2-(n_2-n_3)^2]\Delta^E_{13}(\delta)\ . \tag{4.3}$$

Quite similarly, one finds that the coefficient of $\sin(\delta h)/h^4$ is

$$\mathcal{B}(\delta)=2\pi[(n_1-n_2)^2-(n_1-n_3)^2-(n_2-n_3)^2]\Delta^H_{13}(\delta) \tag{4.4}$$

and the leading asymptotic term is

$$I_{\mathrm{LAT}}(h)=[\mathcal{A}_0+\mathcal{A}(\delta)\cos(\delta h)+\mathcal{B}(\delta)\sin(\delta h)]/h^4\ . \tag{4.5}$$

Thus, an accurate measurement of $I(h)$ in the outermost region of the SAS h's, would allow one to get δ, $\mathcal{A}_0$, $\mathcal{A}(\delta)$, and $\mathcal{B}(\delta)$ by fitting (4.5) to the experimental tail intensity. Moreover, whenever it is possible to change the density of the phase 1 and/or 2, without modifying the internal boundaries $\mathcal{S}_1$ and $\mathcal{S}_2$, one can obtain a new set of values for $\mathcal{A}_0$, $\mathcal{A}(\delta)$, and $\mathcal{B}(\delta)$, which are related to the former ones by Eqs.(4.1), (4.3), and (4.4). Thus, if we know the involved densities, from the two $\mathcal{A}_0$ values, we can determine both $\mathcal{S}_{13}$ and $\mathcal{S}_{23}$. On the contrary, the two determinations of $\mathcal{A}(\delta)$ and $\mathcal{B}(\delta)$ should scale by the same factor, dependent only on the phase densities, as one sees from Eqs. (4.3) and (4.4). In this way, one can partially test whether the former constraint on the invariance of the internal geometry of the sample is met or not.

Let us assume now that the principal curvatures radii of the film are, in absolute value, larger than the film thickness. Accounting for the molecular structure of phase 3, this condition is practically necessary for the phase to appear homogeneous, i.e., that n_3 be constant. From this property, it immediately follows that no hyperbolic contact can take place since, from Eq. (3.5), the Gaussian curvatures of $\mathcal{S}_{13}$ and $\mathcal{S}_{23}$, at correspondent points, will have the same sign. Thus, $\mathcal{B}(\delta)=0$, while $\mathcal{S}_{13}$, $\mathcal{S}_{23}$, and $\mathcal{A}(\delta)$ can be expressed in terms of the area S of the surface $\mathcal{S}$, exactly half-way between the faces of the film and of some corresponding averages of the mean

[18] and of the Gaussian curvature of $\mathcal{S}$. In fact, r_m and R_M, the two curvature radii of $\mathcal{S}$, are related to those of $\mathcal{S}_{13}$ and to those of $\mathcal{S}_{23}$ by the relations

$$R_{1M}=R_M-\delta/2,\quad R_{1m}=R_m-\delta/2\ , \tag{4.6a}$$

and

$$R_{2M}=R_M+\delta/2,\quad R_{2m}=R_m+\delta/2\ , \tag{4.6b}$$

obtained from (3.5). Expressing the infinitesimal surface element dS_1 in terms of its Gaussian curvature $\kappa_1=1/(R_{1m}R_{1M})$ and its spherical image $d\hat{\omega}$, since the latter is equal to that of the set dS, correspondent to dS_1 via the map (3.2), it becomes easy to relate the two surface elements. Using (4.6a), one finds that

$$dS_1=dS_{13}=dS\left[1+\frac{\delta}{2}\left(\frac{1}{R_m}+\frac{1}{R_M}\right)+\frac{\delta^2}{4}\kappa\right]$$

$$\equiv dS(1+H\delta+\kappa\delta^2/4)\ , \tag{4.7}$$

where H is the so-called mean curvature of $\mathcal{S}$ at the relevant point. A similar expression holds true for dS_{23} and by their integration one finds

$$S_{13}=S(1+\langle H\rangle\delta+\langle\kappa\rangle\delta^2/4)\ , \tag{4.8a}$$

$$S_{23}=S(1-\langle H\rangle\delta+\langle\kappa\rangle\delta^2/4)\ , \tag{4.8b}$$

where $\langle H\rangle$ and $\langle\kappa\rangle$ denote the averages over $\mathcal{S}$ of its mean and of its Gaussian curvature, respectively. Due to the assumed existence [24] of an effective free energy involving the mean and the Gaussian curvatures of the interfaces, the possibility of determining the former average quantities appears interesting. However, Eqs. (4.8a) and (4.8b) are not sufficient to this aim because they involve three unknown quantities: S, $\langle H\rangle$, and $\langle\kappa\rangle$. Unfortunately, even exploiting the information contained in $\mathcal{A}(\delta)$, one does not find the required third equation. In fact, using Eq. (4.6), the integrand of Δ_{13}^E [see Eq. (3.13)] becomes

$$R_mR_M(1-\delta^2/4R_m^2)^{1/2}(1-\delta^2/4R_M^2)^{1/2}\ , \tag{4.9}$$

and the evaluation of Δ_{13}^E does not appear possible without knowing the shape of $\mathcal{S}$. Assuming that δ be sufficiently small for (4.9) to be well approximated by its $o(\delta^2)$ expansion, one finds

$$\Delta_{13}^E=S[1-(\langle H^2\rangle-\langle\kappa\rangle/2)\delta^2/2]+O(\delta^4)\ . \tag{4.10}$$

First of all we note that the $o(\delta)$ approximation of Eqs. (4.8) and (4.10) yields

$$S=\Delta_{13}^E$$

and (4.11)

$$\langle H\rangle=(S_{13}-S_{23})/(2\delta\Delta_{13}^E)\ ,$$

so that finding experimentally that $S_{13}=S_{23}$ implies that $\langle H\rangle=0+O(\delta)$. In passing, we recall that recently Auvray *et al.* [25] have already found some microemulsions characterized by a null average mean curvature, essentially by checking that the condition $S_{13}=S_{23}$ turns out experimentally true. Considering now the $O(\delta^2)$ equations, one sees that the appearance of the new quantity $\langle H^2\rangle$ makes the total number of equations still insufficient. In fact, only the quantities

$$S(1+\langle\kappa\rangle\delta^2/4)=(S_{13}+S_{23})/2\ , \tag{4.12a}$$

$$S\langle H\rangle=(S_{13}-S_{23})/(2\delta)\ , \tag{4.12b}$$

$$S\langle H^2\rangle=(S_{13}+S_{23}-2\Delta_{13}^E)/(\delta^2) \tag{4.12c}$$

are fully determined, although the lhs's involve the unknown area S of the half-way surface of the film. However, Eq. (4.12c) is particularly interesting because if one finds that $S_{13}+S_{23}-2\Delta_{13}^E=0$, then one can conclude that $H(r)=0$, i.e., the mean curvature is *locally* equal to zero and thus the aforesaid surface is a minimal surface.

Whenever it is possible to modify the thickness of the film without changing the geometrical configuration of its half-way surface, then one could also determine S. In this case, denoting by δ' the new film thickness, one obtains the new values S'_{13}, S'_{23} and $\Delta_{13}'^E$. These, combined with the former, give six equations, whose solution yields the four quantities

$$S=(S_+\delta'^2-S'_+\delta^2)/(\delta'^2-\delta^2)\ , \tag{4.13a}$$

$$\langle\kappa\rangle=4(S'_+-S_+)/[S(\delta'^2-\delta^2)]\ , \tag{4.13b}$$

$$\langle H\rangle=(S_{13}-S_{23})/2S\delta\ , \tag{4.13c}$$

$$\langle H^2\rangle=2(S_+-\Delta_{13}^E)/S\delta^2 \tag{4.13d}$$

[here $S_+\equiv(S_{13}+S_{23})/2$ and $S'_+\equiv(S'_{13}+S'_{23})/2$] and two constraints

$$(S_{13}-S_{23})/\delta=(S'_{13}-S'_{23})/\delta'\ , \tag{4.14a}$$

$$(S_+-\Delta_{13}^E)/\delta^2=(S'_+-\Delta_{13}'^E)/\delta'^2\ , \tag{4.14b}$$

which have to be obeyed by the determined parameters if the assumptions are really fulfilled. Thus, once the latter turn out to be satisfactorily fulfilled, one succeeds in determining the area and the averages of the Gaussian, of the mean and of the squared mean curvature of the film using only the leading asymptotic term of the scattered intensity.

The case $n_1=n_2\neq n_3$ can be discussed along the same lines. One finds that the resulting equations involve only S_+ and $(n_1-n_3)^2$. Thus, $\langle H\rangle$ never does appear and by changing the phase densities, no new information is obtained from the asymptotic leading term. A necessary condition for $|\delta/R_l|<1$ is that one observes $\mathcal{B}(\delta)=0$. Whenever one would also observe $\mathcal{A}_0=-\mathcal{A}(\delta)$, from the result $\langle H^2\rangle=0$ one would conclude that $H(\mathbf{r})=0$. Clearly this result should be observed [26] in the case of cubic phases [27] since the relevant surface $\mathcal{S}$ is commonly believed to be a minimal surface [28].

V. CONCLUSIONS

Since our analysis focuses upon the behavior of the SAS intensities at high h's, we are not interested in the intensity features commonly observed in the range of low h's as, for instance, those observed in some microemulsions and related to the existence of a typical length scale [29]. Two questions, however, appear quite natural: why use only the leading asymptotic term and how accurately can the asymptotic behavior of SAS intensities be observed? Although no precise *a priori* answers to these questions are presently possible, we would like to make some remarks. Concerning the first question, $I_{\mathrm{LAT}}(h)$ becomes dominant for sufficiently large h regardless of the magnitude of the next term. Moreover, it is also well known that accounting for higher-order terms in an asymptotic expansion generally shifts to larger h's the region where the approximation becomes accurate. Thus, rather optimistically, one could add to the considered $I_{\mathrm{LAT}}(h)$ expression the nonoscillatory contribution, first worked out by Kirste and Porod [30,31],

$$\pi \sum_{\substack{i,j=1 \\ j>i}}^{M} \frac{(n_i-n_j)^2 S_{ij}(3\langle H^2\rangle - \langle \kappa \rangle)}{h^6} ,$$

using the argument that the sum of the asymptotic oscillatory contributions, decreasing as $h^{-\beta}$ with $4<\beta<6$ (whose existence appears possible according to the analysis of [31]), averages to zero. However, we do not believe that this argument can also be invoked in order to discard [32] the $O(h^{-4})$ oscillatory contribution (4.5), since the latter is determined by all the coating films. Actually, for the mathematical reason mentioned above, we think that $I_{\mathrm{LAT}}(h)$ should yield the most accurate asymptotic expression, although the experimental determination of the latter is not easy, in general. In fact, one can expect that the corresponding asymptotic behavior sets in when $\delta h \geq 2\pi$. Considering a film thickness of 10 Å, one concludes that the intensity must accurately be measured at $h \approx 0.6$ Å^{-1}. Thus, we are in h region where the density fluctuations, internal to each bulk phase, can become important enough to invalidate Debye's assumption. However, for thicker films, the situation becomes more manageable and, moreover, some useful information can also be obtained from the measurement of the Porod invariant and from the known sample stoichiometry. For these reasons, knowing that the general expression of the leading asymptotic behavior of SAS intensities is given by Eq. (1.1) will certainly be of help in the analysis of experimental results, as it has already happened in some cases [4].

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[16] Instead of $\mathcal{H}_j(\mathbf{r}_i,0,0)$ we use the simpler notation $\mathcal{H}_j(\mathbf{r}_j)$. Moreover, $\mathrm{sgn}(F_{j,xx}+F_{j,yy})$ is equal to the sign of the trace of the matrix appearing in (2.8) at $x=y=0$ and coincides with the sign of $F_j(x,y)$ around the origin.
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[22] Note that by this way of doing one assumes that the integral on the rhs of (2.1) be written as $\int_{-\infty}^{\infty} \gamma_1(r)\sin(hr)dr$, with $\gamma_1(r) \equiv r\gamma(r)$ when $r>0$ and $\gamma_1(r) \equiv 0$ when $r<0$.
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