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Correlation functions of amorphous multiphase systems

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We give two general integral expressions for the first and second derivatives of the so-called stick probability functions which are commonly used in analyzing x-ray-scattering results. Then it is shown that by letting the length of the stick go to zero, the limit of the second derivative can be expressed in terms of an integral over the singularity lines of the surfaces which separate the different phases of the sample. In this way one has achieved the generalization of the well-known result that the limit of the second derivative is always zero when phase boundaries are smooth.

I. INTRODUCTION

Light or x-ray scattering experiments are one of the most powerful tools for investigating the underlying texture of materials. Indeed, according to the experimental apparatus one uses, they allow one to obtain precise information on the arrangement of the atoms in condensed matter or to evaluate the specific separation surfaces for multiphase systems. It is well known that the knowledge of the last parameter is very important for those solid systems, whose distinctive property reflects mainly the interactions between contiguous environments.

Let us briefly recall how information is obtained from the measured scattered intensity. For the sake of generality, we assume that our material sample is made up of N different phases. Each of these, characterized by the index i, has an electronic density $n_i(\vec{r})$ and occupies a spatial set $\underline{V}_i$, whose volume is denoted by V_i.[1] The total average density $\bar{n}$ will be

$$\bar{n} = \sum_{i=1}^{N} \frac{1}{V} \int_{\underline{V}_i} n_i(\vec{r}) d\vec{r} , \tag{1.1}$$

where V is the volume of the sample set $\underline{V}$, i.e., $\underline{V} = \cup_{i=1}^{N} \underline{V}_i$.

It is useful to introduce the local fluctuation density function

$$\eta_i(\vec{r}) \equiv \begin{cases} n_i(\vec{r}) - \bar{n} & \text{if } \vec{r} \in \underline{V}_i \\ 0 & \text{if } \vec{r} \notin \underline{V}_i \end{cases} \tag{1.2}$$

and then the global correlation function

$$\gamma(\vec{r}) \equiv \sum_{i,j=1}^{N} \frac{1}{V} \int_{\underline{V}_j} d\vec{r}_0 \eta_i(\vec{r}_0 + \vec{r}) \eta_j(\vec{r}_0) / \langle \eta^2 \rangle , \tag{1.3}$$

where

$$\langle \eta^2 \rangle \equiv \sum_{j=1}^{N} \frac{1}{V} \int_{\underline{V}} \eta_j^2(\vec{r}) d\vec{r} . \tag{1.4}$$

According to classical theory,[2] the scattering intensity $i(\vec{k})$ is given by

$$i(\vec{k}) \equiv \sum_{i,j=1}^{N} \int_{\underline{V}} d\vec{r}_1 \int_{\underline{V}} d\vec{r}_2 \eta_i(\vec{r}_1) \eta_j(\vec{r}_2) \exp(i\vec{k} \cdot \vec{r}_{12}) , \tag{1.5}$$

where $\vec{r}_{12} \equiv \vec{r}_1 - \vec{r}_2$ and $\vec{k} \equiv \vec{k}_1 - \vec{k}_2$ is the difference vectors between ingoing and outgoing wave vectors. Comparison with Eq. (1.3) yields the fundamental relation

$$i(\vec{k}) = V \langle \eta^2 \rangle \int_{\underline{V}} e^{i\vec{k} \cdot \vec{r}} \gamma(\vec{r}) d\vec{r} , \tag{1.6}$$

which relates the scattered intensity to the Fourier transform of the correlation function. If we assume that our system is isotropic, the correlation function and the scattered intensity will depend only on r and k, respectively. In particular, Eq. (1.5) takes the simpler form

$$i(k) = 4\pi V \langle \eta^2 \rangle \int_0^{\infty} r^2 \gamma(r) \frac{\sin kr}{kr} dr , \tag{1.7a}$$

while its inverse integral transform is

$$\gamma(r) = \frac{1}{2\pi^2 V \langle \eta^2 \rangle} \int_0^{\infty} k^2 i(k) \frac{\sin kr}{kr} dk . \tag{1.7b}$$

Clearly, through Eq. (1.6) or (1.7), according to the particular case one is concerned with, one can obtain the information we have given at the beginning. One possibility is to hypothesize a particular spatial distribution for the scatterers, that is, to evaluate the "theoretical" scattering intensity by Fourier-transforming the resulting correlation function and finally to compare this intensity with the experimental one. If the agree-

ment turns out to be satisfactory, then one can confidently conclude that the spatial configuration one has chosen at the start is fairly close to the real one. With this procedure it has been possible, for instance, to get accurate information on the structure of pure liquids and of electrolytic solutions.[3]

In this paper we shall be concerned with a different approach, which consists of finding out direct connections between the correlation function and some physical quantities of the sample as well as getting the explicit form of correlation functions through the use of some general and apparently mild hypotheses. Two celebrated examples are, respectively, the Debye[4]-Porod[5] relation and the Debye definition of "random" system. The first result, which is of paramount importance in small-angle x-ray scattering, states that the value of the derivative of the correlation function at the origin [i.e., $\dot{\gamma}(0)$] is proportional to the specific surface (i.e., the ratio between the total phases separating surface and the total volume of the sample). The second result shows that for random two-phase systems, the correlation function is a simple exponential function. Both these results have been generalized by Peterlin[6] and by Brumberger and Goodisman[7] to N-component systems. However, while the first generalization appears quite safe, it has been noted recently[8] that the second one leads to the following, rather puzzling consequence: It is not generally possible to recover the correlation function of a two-phase random system from the correlation function of a three-phase random one, once we have made the two phases of the last system equal. This result clearly indicates the necessity of a more thorough investigation of the "randomness" hypothesis by looking more carefully at the connection between this hypothesis and the approximations performed in obtaining the previous results.

In this paper, we report the first results that we obtained by looking at these problems with the above-mentioned motivation in mind. In particular, we shall show that the first- and the second-order derivatives of the correlation function [$\dot{\gamma}(r)$ and $\ddot{\gamma}(r)$, respectively] can be expressed through integral formulas which are mainly related to the boundaries of the scatterers. Then by evaluating the limit of these expressions as $r \to 0$ we shall get the well known Debye-Porod relation and the generalization of the result found a long time ago by Kirste and Porod[9] for smooth particles only.

In fact, we will show that when the boundaries of the phases are sufficiently regular (in practice, the tangent plane exists at any boundary point), then $\ddot{\gamma}(0)=0$, while when we have lines of singularities, such as sharp edges or lines where at least three phases meet, then $\ddot{\gamma}(0)$ is different from zero. Indeed the value of $\ddot{\gamma}(0)$ is related to the integral of a known weight function along the singularity lines.

The paper is organized as follows. In the next section we shall give the main definition as well as the integral expression of the first-order derivative of the correlation function. In the Sec. III we report the integral expression of the second-order derivative and we sketch the proof that $\ddot{\gamma}(0)=0$ for the regular-surface case. In the Sec. IV we give the value of $\ddot{\gamma}(0)$ for the more general cases, namely, when physical singularities of the boundaries are allowed. Finally, a few technical details are discussed in Appendixes A and B.

II. THE FIRST-ORDER DERIVATIVE OF THE "STICK-PROBABILITY FUNCTIONS"

Before introducing these quantities, we must recall that our sample's idealization explicitly assumes that any constituting piece behaves as a homogeneous medium. By this we mean that the relevant electronic density $\eta_i(\vec{r})$ takes the same value at any point P inside the chosen ith phase. Hence the value of $n_i(\vec{r})$ is either zero, when P (i.e., the point whose position vector is $\vec{r}_i$) does not lie in the region occupied by the ith phase, or n_i, when P does. Therefore if we recall the definition of the characteristic function $\rho_{\underline{V}}(P)$ of a set $\underline{V}$,

$$\rho_{\underline{V}}(P)=\begin{cases}1 & \text{when } P\in\underline{V}\\ 0 & \text{when } P\notin\underline{V},\end{cases} \tag{2.1}$$

we immediately realize that

$$n_i(\vec{r})=n_i\rho_{\underline{V}_i}(\vec{r})\,. \tag{2.2}$$

Then all quantities defined in the preceding section can be written in terms of the set characteristic functions. In fact, the local fluctuation function $\eta_i(\vec{r})$ defined by Eq. (1.2) becomes

$$\eta_i(\vec{r})=(n_i-\bar{n})\rho_{\underline{V}_i}(\vec{r})\,, \tag{2.3}$$

while from Eq. (1.1) we immediately have the average electron density

$$\bar{n}=\sum_1^N \phi_i n_i \tag{2.4}$$

in terms of the ith-phase volume fraction $\phi_i \equiv V_i/V$. Similarly, from Eqs. (1.4) and (1.3) we get, respectively,

$$\langle\eta^2\rangle=\sum_1^N (n_i-\bar{n})^2\phi_i \tag{2.5}$$

and

$$\gamma(\vec{r}) = \sum_{i,j=1}^{N} \frac{(n_i - \bar{n})(n_j - \bar{n})}{\langle \eta^2 \rangle} \mathfrak{P}_{ij}(\vec{r}) , \tag{2.6}$$

where we have set

$$\mathfrak{P}_{ij}(\vec{r}) \equiv \frac{1}{V} \int d\vec{r}_1 \rho_{\underline{V}_i}(\vec{r}_1) \rho_{\underline{V}_j}(\vec{r}_1 + \vec{r}) . \tag{2.7}$$

For the support properties of the two characteristic functions which appear in the integrand of Eq. (2.7), the integration region can be the Euclidean three-dimensional space or the $\underline{V}$ set. From Eq. (2.6) one sees that the knowledge of $\mathfrak{P}_{ij}$'s implies that of the correlation function, while Eq. (2.7) clearly shows the importance of the geometrical aspect in the definition of the $\mathfrak{P}_{ij}(\vec{r})$.

So far we have not taken into account that our sample is an amorphous system. The last property implies that any anisotropic effect must disappear when the sample becomes infinitely large. Therefore the sample's infinite volume limit of $\mathfrak{P}_{ij}(\vec{r})$ must be always the same whatever the direction of $\vec{r}$; hence

$$\lim_{V \to \infty} \mathfrak{P}_{ij}(\vec{r}) = \tilde{P}_{ij}(r) . \tag{2.8}$$

Moreover, the angular average of $\mathfrak{P}_{ij}(\vec{r})$ over all possible directions $\hat{\omega}$ of $\vec{r}$

$$P_{ij}(r) = \int \mathfrak{P}_{ij}(r\hat{\omega}) \frac{d\hat{\omega}}{4\pi} \tag{2.9}$$

in the infinite-volume limit must be equal to the previous function

$$\lim_{V \to \infty} P_{ij}(r) = \tilde{P}_{ij}(r) . \tag{2.10}$$

Since our subsequent analysis deals only with $P_{ij}(r)$ functions, it follows that the results we get will refer to the angular average of the correlation functions,

$$\gamma(r) = \sum_{i,j=1}^{N} \frac{(n_i - \bar{n})(n_j - \bar{n})}{\langle \eta^2 \rangle} P_{ij}(r) , \tag{2.11}$$

so that they hold true not only for isotropic systems but to a certain extent also for anisotropic ones. The positive-value functions

$$P_{ij}(r) \equiv \frac{1}{4\pi V} \int d\vec{r}_i \int d\hat{\omega} \, \rho_{\underline{V}_i}(\vec{r}_i) \, \rho_{\underline{V}_j}(\vec{r}_i + r\hat{\omega}) \tag{2.12}$$

have been introduced in Ref. 4 and they will be called "stick-probability functions" or more simply, probability functions. The reason for this nomenclature is the following. Let us toss at random a stick of length r for a very large number of times and let us ask how many times we find one end of the stick, say A, in the set $\underline{V}_i$ and the other end in the set $\underline{V}_j$. The ratio of these two numbers represents the probability for the last configuration when the toss number increases indefinitely. One can easily convince oneself that $P_{ij}(r)$, defined by Eq. (2.12), represents exactly this probability. In fact, the probability that the end A of the stick falls inside the set of measure $d\vec{r}_i$, located at the point $\vec{r}_i$ inside the set $\underline{V}_i$, is equal to the ratio of favorable cases $\propto d\vec{r}_i \rho_{\underline{V}_i}(\vec{r}_i)$ to the total number of cases $\propto V$; hence it is $\rho_{\underline{V}_i}(\vec{r}_i) d\vec{r}_i / V$.

Now we require that the B end falls inside V_j and the stick's orientation is $\hat{\omega}$. According to the principle of conditional probabilities, in order to get the total probability, we must multiply the probability evaluated above by the probability of the last event, i.e., $\rho_{\underline{V}_j}(\vec{r}_i + r\hat{\omega}) d\hat{\omega}/4\pi$.

By summing over all favorable cases we end up with Eq. (2.12) and thus we can correctly refer to $P_{ij}(r)$ as the stick-probability function relevant to the ith and jth phases. Moreover, by following this interpretation one immediately recognizes that the result of the angular integration in Eq. (2.12) is equal to the value of the solid angle of the intersection set between $\underline{V}_j$ and the sphere $\underline{B}(\vec{r}_i, r)$ whose center lines at $\vec{r}_i$ and whose radius is r. For later convenience, we shall denote by $\underline{\Omega}_j(\vec{r}_i, r)$ the corresponding solid-angle set (i.e., the set obtained by projecting the previously defined intersection set on the unit-radius sphere with center at $\vec{r}_i$) and by $\Omega_j(\vec{r}_i, r)$ the measure of the latter.

Then we immediately have

$$P_{ij}(r) = \frac{1}{4\pi V} \int_{\underline{V}_i} d\vec{r}_i \Omega_j(\vec{r}_i, r) . \tag{2.13}$$

However, this expression can also be written in the following way:

$$P_{ij}(r) = \frac{1}{4\pi V} \int_{\underline{V}_i} d\vec{r}_i \int_{\underline{V}_j} d\vec{r}_j \int d\hat{\omega} \, \delta(\vec{r}_i + r\hat{\omega} - \vec{r}_j) , \tag{2.14}$$

where the Dirac function clearly accounts for the fact that the distance between the two points $\vec{r}_i$ and $\vec{r}_j$, which are inside the ith and the jth phase, respectively, must be equal to r. The use of Eq. (2.14) makes the accomplishment of our first task very easy, namely, to obtain the integral expression of the 1st derivative of $P_{ij}(r)$.

In fact, the increment of the stick-probability function when the stick's length is increased by Δr is given by

$$\Delta P_{ij}(r) = \frac{1}{4\pi V} \int_{\underline{V}_i} d\vec{r}_i \int_{\underline{V}_j} d\vec{r}_j \int d\hat{\omega} [\delta(\vec{r}_i + \hat{\omega}(r + \Delta r) - \vec{r}_j) - \delta(\vec{r}_i + \hat{\omega} r - \vec{r}_j)] . \tag{2.15}$$

By handling the Dirac function as an ordinary function, we apply Lagrange's theorem for obtaining

$$\delta(\vec{r}_i+\hat{\omega}(r+\Delta r)-\vec{r}_j)-\delta(\vec{r}_i+\hat{\omega}r-\vec{r}_j)$$
$$=\Delta r(\hat{\omega}\cdot\nabla)\delta(\vec{r}_i+\hat{\omega}r+\xi\hat{\omega}\Delta r-\vec{r}_j)\,, \quad (2.16)$$

where ξ is a suitable positive number which does not exceed 1. Since the differential operator on the right-hand side (rhs) of Eq. (2.16) can be thought of as acting on the variables $\vec{r}_i$, and since $\hat{\omega}$ does not depend on the latter, the rhs of Eq. (2.16) is the divergence of the vectorial field

$$\hat{\omega}\delta(\vec{r}_i+\hat{\omega}r+\xi\hat{\omega}\Delta r-\vec{r}_j)\,.$$

Hence, after substituting Eq. (2.16) into Eq. (2.15) we can apply the Gauss theorem and obtain

$$\Delta P_{ij}(r)=\frac{\Delta r}{4\pi V}\int d\hat{\omega}\int_{\underline{V}_j}d\vec{r}_j\int_{\underline{S}_i}dS_i\hat{\sigma}_i\cdot\hat{\omega}$$
$$\times\delta(\vec{r}_i+\hat{\omega}r+\xi\hat{\omega}\Delta r-\vec{r}_j)\,, \quad (2.17)$$

where $\underline{S}_i$ denotes the boundary set of $\underline{V}_i$ and $\hat{\sigma}_i$ is the unit vector perpendicular at the surface $\underline{S}_i$ in the point $\vec{r}_i$, to which the differential element dS_i refers. Moreover, $\hat{\sigma}_i$ lies outside the set $\underline{V}_i$.

By taking the limit $\Delta r\to 0$ we arrive at the desired result

$$\dot{P}_{ij}(r)=\frac{1}{4\pi V}\int d\hat{\omega}\int_{\underline{V}_j}d\vec{r}_j\int_{\underline{S}_i}dS_i\hat{\sigma}_i\cdot\hat{\omega}\delta(\vec{r}_i+\hat{\omega}r-\vec{r}_j)\,, \quad (2.18)$$

which can be also written

$$\dot{P}_{ij}(r)=\frac{1}{4\pi V}\int_{\underline{S}_i}dS_i\int_{\underline{\Omega}_j(\vec{r}_i,r)}d\hat{\omega}\,\hat{\sigma}\cdot\hat{\omega}\,. \quad (2.19)$$

The derivation of the last result is mathematically meaningful, provided the boundary $\underline{S}_i$ is such that at any of its points it allows for the existence of the tangent plane. Of course, we assume also that the measure of $\underline{S}_i$ is finite, as far as V is finite. We must also note that the rhs of Eq. (2.19) makes sense also when the boundary $\underline{S}_i$ contains a set of singular points (i.e., points where the tangent plane does not exist), provided the last points can be included into closed sets whose measure can be made arbitrarily small.

The integral expression that we have obtained for the first derivative of the stick probability is very useful for understanding the mathematical approximations which Debye and co-workers implicitly did when they got the correlation function for "random" systems. We shall leave this discussion to a further paper, but before attempting the evaluation of the second derivative we would like to show how the generalized Debye-Porod result on specific surfaces immediately follows from Eq. (2.19).

To this aim we must evaluate the limit of $\dot{P}_{ij}(r)$, as $r\to 0$, which will be denoted by $\dot{P}_{ij}(0)$. Let us refer to a general point P_i belonging to $\underline{S}_i$. If we consider a sufficiently small spherical neighborhood of P_i, $\underline{B}(\vec{r}_i,\delta)$, we meet with one of the following cases: (a) no jth phase is contained in $\underline{B}$, (b) only the ith and the jth phases are contained in $\underline{B}$, and finally (c) besides these two phases there is at least another phase in $\underline{B}$. In the first case, we find that $\underline{\Omega}_j(\vec{r}_i,r)\equiv\varnothing$ (null set) for any r smaller than $\underline{B}$ radius δ; in the second case since by hypothesis $\underline{S}_i$ has a tangent plane at $\vec{r}_i$, $\underline{\Omega}_j(\vec{r}_j,r)$ as $r\to 0$ becomes a half sphere; in the third case, the value of the limit of $\underline{\Omega}_j(\vec{r}_i,r)$ will depend on the particular configuration. However, on physical grounds the set of points P_i where more than two phases meet is extremely small. This implies that the measure of the last set is zero. Hence we get

$$\dot{P}_{ij}(0)=\frac{1}{4\pi V}\int_{\underline{S}_{ij}}dS_i\int_{\underline{\Omega}_j(\vec{r}_i,0^+)}d\hat{\omega}\,\hat{\sigma}_i\cdot\hat{\omega}\,, \quad (2.20)$$

where $\underline{S}_{ij}$ is the surface set which separates the ith from the jth phase and $\underline{\Omega}_j(\vec{r}_i,0^+)$ is the unit radius half sphere. Once we have recalled that $\hat{\omega}$, like $\hat{\sigma}_i$, goes from the ith to the jth phase, and that $\hat{\sigma}_i$ represents the top point of the half sphere, the evaluation of the last integral gives as a result π. In this way we obtain

$$\dot{P}_{ij}(0)=\frac{S_{ij}}{4V}\quad(i\neq j)\,, \quad (2.21a)$$

which generalizes to N-component systems the result found by Debye and Porod for two-component ones.[10] We remark that the result given by Eq. (2.21a) is not new, since it has been achieved by Goodisman and Brumberger[7] and by Peterlin[6] with a procedure different from ours but quite similar to Debye's one. Finally, the evaluation of $\dot{P}_{ii}(0)$ can be performed along the same line, with the obvious differences that $\hat{\sigma}_i$ points toward the opposite direction of the half sphere's top point and that all S_i surfaces will contribute. Thus one finds

$$\dot{P}_{ii}(0)=-\frac{S_i}{4V}\,. \quad (2.21b)$$

Finally, by substituting Eq. (2.19) or Eqs. (2.21a) and (2.21b) into Eq. (2.11), one obtains the value of $\dot{\gamma}(0)$ in the most general case:

$$\dot{\gamma}(0)=\sum_{i,j=1}^{N}\frac{(n_i-\bar{n})(n_j-\bar{n})}{4V\langle\eta^2\rangle}S_{ij},$$

where $S_{ii}\equiv -S_i$.

III. THE SECOND-ORDER DERIVATIVE

The second-order derivative of $P_{ij}(r)$ can also be expressed in terms of a suitable integral on the relevant phase boundaries. In order to arrive at this formula one could start from Eq. (2.18) and parallel the same procedure which led us from Eq. (2.14) to Eq. (2.18). In this way, one obtains the result

$$\ddot{P}_{ij}(r)=-\frac{1}{4\pi V}\int d\hat{\omega}\int_{\underline{S}_i}dS_i\int_{\underline{S}_j}dS_j(\hat{\sigma}_i\cdot\hat{\omega})(\hat{\sigma}_j\cdot\hat{\omega})\times\delta(\vec{r}_i+r\hat{\omega}-\vec{r}_j),\quad(3.1)$$

where the meaning of symbols involved is the same as that explained after Eq. (2.17) and the minus sign in front of the rhs follows from the fact that the del operator ∇ has been converted to the operator ∇_j which acts on the variables $\vec{r}_j$.

Although quite elegant, Eq. (3.1) is not very convenient for calculations because the integration of the δ function requires the application of the general theory of distributions defined on regular surfaces[11] or an appropriate change of integration variables, which in general is not easy to obtain.

However, one succeeds in eliminating the δ function in Eq. (3.1) by following a different approach. To this aim, we start from Eq. (2.19). The increment of $\dot{P}_{ij}(r)$, induced by the variation Δr of the stick's length, will be

$$\Delta\dot{P}_{ij}(r)=\frac{1}{4\pi V}\int_{\underline{S}_i}dS_i\left(\int_{\underline{\Omega}_j(\vec{r}_i,r+\Delta r)}(\hat{\sigma}_i\cdot\hat{\omega})d\hat{\omega}-\int_{\underline{\Omega}_j(\vec{r}_i,r)}(\hat{\sigma}_i\cdot\hat{\omega})d\hat{\omega}\right),\quad(3.2)$$

namely,

$$\Delta\dot{P}_{ij}(r)=\frac{1}{4\pi V}\int_{\underline{S}_i}dS_i\int_{\underline{\Delta\Omega}_j(\vec{r}_i,r)}(\hat{\sigma}_i\cdot\hat{\omega})d\hat{\omega},\quad(3.3)$$

where $\underline{\Delta\Omega}_j(\vec{r}_i,r)$ denotes the difference set between $\underline{\Omega}_j(\vec{r}_i,r+\Delta r)$ and $\underline{\Omega}_j(\vec{r}_i,r)$. With reference to Fig. 1, $\underline{\Delta\Omega}_j$ is composed of the tips of all those vectors $\hat{\omega}$ whose directions fall into the shaded region. Moreover, when Δr goes to zero, the measure $\Delta\Omega_j(r_i,r)$ of $\underline{\Delta\Omega}_j$ also goes to zero. Therefore in order to get the second derivative $\ddot{P}_{ij}(r)$, we must evaluate

$$\Delta I=\int_{\underline{\Delta\Omega}_j(r_i,r)}d\hat{\omega}(\hat{\sigma}_i\cdot\hat{\omega})\quad(3.4)$$

up to terms $O(\Delta r)$.[12] To this aim, let us choose a point, say A, on the "external" contour $\underline{\Gamma}_d$, $AA''A'$, which must be also thought of as possessing orientation, and let P be a particular point on it. Of course, we can associate with any point $P\in\underline{\Gamma}_d$ a real number l, which corresponds to the length of the oriented arc AP. Moreover, let $\Delta n(l)$ denote the length of the segment PQ_1, which is perpendicular to the curve $\underline{\Gamma}_d$ at the point P and which intersects the projected curve $\underline{\Gamma}_p$ at the point Q_1. (See Fig. 2, where the spatial configuration around P is reported in a more detailed way. Besides, its caption also gives the precise definition of the symbols we shall use in the following.) Clearly up to terms $O(\Delta r)$, we obtain

$$\Delta I=-\int_{\underline{\Gamma}_d}\frac{dl\,\Delta n(l)}{r^2}[\hat{\sigma}_i\cdot\hat{\omega}(l)]+O(\Delta r),\quad(3.5)$$

where the integral is evaluated along the curve $\underline{\Gamma}_d$, depicted in Fig. 1. One should also note the reported dependence of $\hat{\omega}$ on the curvilinear abscissa l, which is, of course correct only up to

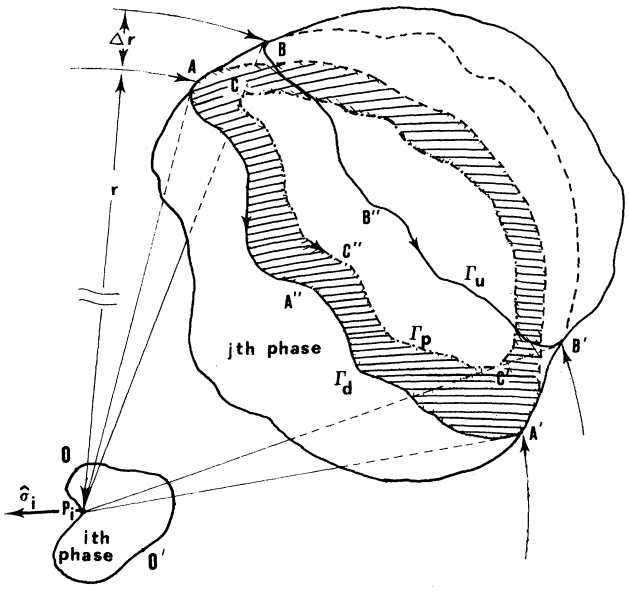

FIG. 1. $ABB'A$ and $00'$ denote the frontal views of two regions which are filled up by jth and ith phases, respectively. Moreover, the arcs AA' and BB' denote the corresponding intersections with P_i-centered spheres of radii r and $r+\Delta r$, respectively. In addition, $BB''B'$ and $AA''A'$ represent the contours of the intersection sets between the previous two spheres and the considered jth-phase region. The contour $CC''C'$ is the projection of the contour $BB''B'$ on the sphere of radius r. The curves $AA''A'$, $BB''B'$, and $CC''C'$ will be denoted by Γ_d, Γ_u and Γ_p. Finally, the set of all unit vectors $\hat{\omega}$ which give the directions of straight half lines, leaving from P_i and crossing the shaded region, corresponds to $\underline{\Delta\Omega}_j(\vec{r}_i,\Delta r)$.

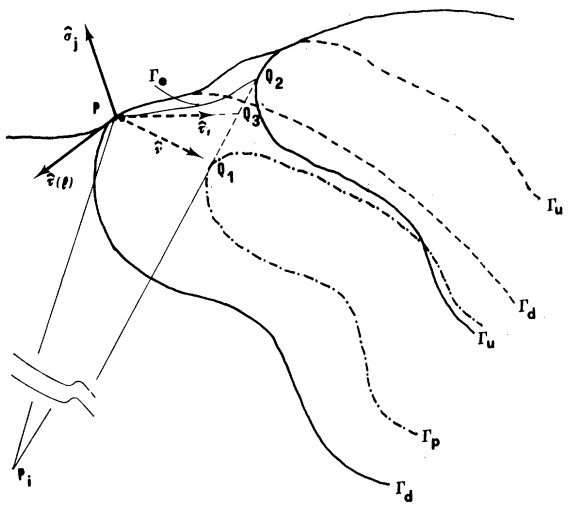

FIG. 2. Enlarged view of the spatial configuration of intersections sets in a neighborhood of a general point P_i. The meaning of symbols involved is as follows. $\underline{B}(\vec{r}_i, r)$ is a sphere with a center at $\vec{r}_i$ and radius r, $\underline{\Gamma}_d \equiv \underline{S}_j \cap \underline{B}(\vec{r}_i, r)$, $\underline{\Gamma}_u \equiv \underline{S}_j \cap \underline{B}(\vec{r}_i, r+\Delta r)$, $\underline{\Gamma}_p$ is the projection set through P_i of $\underline{\Gamma}_u$ upon $\underline{B}(\vec{r}_i, r)$. $\hat{\tau}(l)$ is the unit vector of the line tangent to $\underline{\Gamma}_d$ at the point P, whose curvilinear coordinate is l; $\hat{\nu}(l)$ is the unit vector perpendicular to $\hat{\tau}(l)$ and tangent to $\underline{B}(\vec{r}_i, r)$; $\hat{\sigma}_j(l)$ is the unit vector perpendicular to $\underline{S}_j$ at the point P; π is the plane defined by the points P_i and P and by $\hat{\nu}(l)$; $\hat{\tau}_1(l)$ is the vector of the straight line tangent to $\underline{S}_j$ at the point P and lying on the plane π; $\underline{\Gamma}_e \equiv \underline{S}_j \cap \pi$; Q_1 is the point belonging to $\pi \cap \underline{\Gamma}_p$ and nearest to P; Q_2 is the projection of Q_1 on $\underline{\Gamma}_u$; Q_3 is the intersection of the straight line leaving P along the direction $\hat{\tau}_1(l)$ with Q_1Q_2. Finally, we note that this line is also tangent to $\underline{\Gamma}_e$ at P.

terms $O(\Delta r)$.

We must now relate $\Delta n(l)$ to Δr. With reference to Fig. 2, let us call Q_2 the projection on $\underline{\Gamma}_u$ of the point Q_1. We denote respectively by $\hat{\tau}(l)$, $\hat{\nu}(l)$, and $\hat{\tau}_1(l)$ the unit vectors of the tangent to $\underline{\Gamma}_d$ of that normal to $\hat{\tau}(l)$ which lies on the plane tangent to the spherical surface $\underline{B}(\vec{r}_i, r)$ and finally of the tangent to the curve $\underline{\Gamma}_e$, which is determined as the intersection of the surface $\underline{S}_j$ with the plane which passes through the points P, Q_1, and P_i (i.e., the point on S_i whose position vector is $\vec{r}_i$). Q_3 will denote the intersection of the line, which leaves P along the direction $\hat{\tau}_1$, with the segment Q_1Q_2.

We assume that the boundaries $\underline{S}_j$, which we are dealing with, are C_2 functions,[13] namely, that the parametric equations of the boundaries are at least doubly differentiable functions and moreover that the previous equations and the resulting derivatives are continuous functions. When the last condition is fulfilled we are sure that the intersection of $\underline{S}_i$ with any C_2 surface will be certainly a continuous and doubly differentiable curve. Turning back to Fig. 2 one sees that $Q_1Q_2 = \Delta r$, while Q_1Q_3 denotes the differential of the function which represents the curve $\underline{\Gamma}_e$ and then $Q_1Q_3 = \Delta r + O(\Delta r)$. From the triangle PQ_1Q_3, rectangular in Q_1, we have

$$\Delta n(l) \tan\Phi_j(l) = \Delta r + O(\Delta r)\,, \tag{3.6}$$

where Φ_j is the angle between $\hat{\nu}_\tau$ and $\hat{\tau}_1$ or between $\hat{\sigma}_j$ and $\hat{\omega}(l)$.[14]

By substituting this result into Eq. (3.5) and hence into Eq. (3.3), we can immediately evaluate the limit of $(\Delta \dot{P}_{ij}/\Delta r)$ as $\Delta r \to 0$. Therefore the final expression for the second derivative of $P_{ij}(r)$ is

$$\ddot{P}_{ij}(r) = -\frac{1}{4\pi V r^2} \int_{\underline{S}_i} dS_i \int_{\underline{\Gamma}_j(\vec{r}_i, r)} dl\,[\hat{\sigma}_i \cdot \hat{\omega}(l)] \cot\Phi_j(l)\,, \tag{3.7}$$

where the second integral is performed along the curve $\underline{\Gamma}_j(\vec{r}_i, r)$, which is on the surface $\underline{S}_j$ and is such that the distance of any of its points from P_i $(\equiv \vec{r}_i)$ is r.

We must now evaluate the limit of $\ddot{P}_{ij}(r)$ as $r \to 0$. Since $\underline{\Gamma}_j(\vec{r}_i, r)$, provided it does exist, must lie on a sphere of radius r, it is evident that its length goes to zero when $r \to 0$. Moreover, the assumed continuity of $\underline{\Gamma}_j(\vec{r}_i, r)$ with respect to $\vec{r}_i$ and r also implies that $\hat{\omega}(l)$ as $r \to 0$ approaches a unit vector which lies on the plane tangent to the surface $\underline{S}_{ij}$ at the point $\vec{r}_i$. Hence $\hat{\sigma}_i \cdot \hat{\omega}(l) \to 0$ as $r \to 0$. At the same time $\hat{\sigma}_j(l)$, which is the unit vector perpendicular to $\underline{S}_{ij}$ at the point $P(l)$ at a distance r from $\vec{r}_i$, as $r \to 0$, will approach $\hat{\sigma}_i$ for the continuity of the boundary. Hence also $\hat{\sigma}_j(l) \cdot \hat{\omega} \to 0$. In conclusion, as $r \to 0$ the limits of the two factors inside the second integral of (3.7) are both zero and also the integration interval tends to zero. Moreover, the continuity of the partial derivative of the boundary assures us that any of these factors is at least $O(r)$ (for a more detailed proof, see Appendix A) and thus we can conclude that the limit is zero, i.e.,

$$\lim_{r \to 0} \ddot{P}_{ij}(r) = 0\,. \tag{3.8}$$

In this way we have achieved a different proof of the result found for the first time by Kirste and Porod.[9]

IV. THE LIMIT OF THE SECOND-ORDER DERIVATIVE WHEN SHARP EDGES ARE PRESENT

Although the result (3.8) holds true for apparently quite general surfaces, the regularity conditions required for its validity are rarely fulfilled by the boundaries of real multiphase systems. In fact, in order to arrive safely at Eq. (3.7) it has been

necessary to assume that at any point of the set $\underline{S}_{ij}$, the tangent plane exists. Then, we must exclude phase-separating surfaces such as cubes, cylinders, and, more generally, all surfaces with sharp edges, because in these cases tangent planes do not exist at any boundary point. In addition, let us consider a system made up by N phases with $N \geq 3$. In general, there is no reason for excluding the condition that more than two phases meet along a given line. In such cases, at least one of the separating surfaces must have a sharp edge along the line of contact. Therefore if we want the regularity conditions, necessary for the validity of result (3.8), to be fulfilled by N-component systems, it is necessary that any of its connected regions, occupied by a given phase, be immediately surrounded by one and only one phase.

According to this discussion, on the one hand, it appears clear that the most likely configurations of real-system boundaries violate the previous conditions and then that the limit of $\ddot{P}_{ij}(r)$, as $r \to 0$, will be generally found different from zero. On the other hand, one should also expect that this limit must be somehow related to the singularities of the separating surfaces. In order to find out this relation, we must, first of all, understand at which point the proof of relation (3.8) breaks down. To this aim, we shall start by considering the simplest discontinuity we can encounter. It corresponds to the case depicted in Fig. 3. There, the jth-phase wedge, delimited by the half planes $\underline{\pi}_2$ and $\underline{\pi}_3$, and the ith-phase wedge, limited by the half planes $\underline{\pi}_1$ and $\underline{\pi}_4$, share the common edge AA', whose length is $2L$. From the figure one realizes that the contour $\underline{\Gamma}_j(\vec{r}_i, r)$, which appears in Eq. (3.7) and which refers to the point $P_i \equiv C_1$, is composed of curves $\underline{\Gamma}_2$ and $\underline{\Gamma}_3$ on the half planes $\underline{\pi}_2$ and $\underline{\pi}_3$, respectively. Since on these curves, which actually are arcs of circles, the integrand of Eq. (3.7) is almost everywhere well defined—we must, in fact, only exclude the two points H_1 and H_2—we conclude that the integral over $\underline{\Gamma}_2 \cup \underline{\Gamma}_3$ is a function of P_i. Therefore one expects that $\ddot{P}_{ij}(r)$ does exist provided (i) S_i is finite, (ii) the singularities are simply edges or vertices, and (iii) r is different from zero.

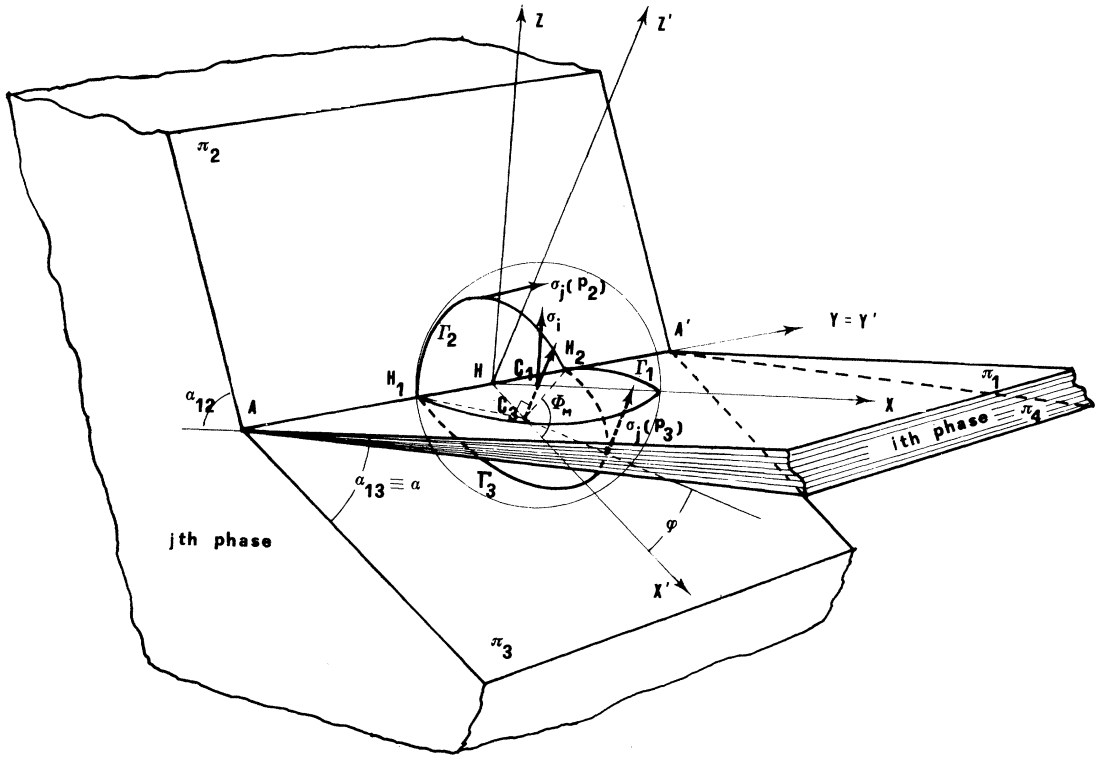

FIG. 3. Spatial configuration of two wedges filled by ith and jth phases and delimited by the half planes $\underline{\pi}_4$ and $\underline{\pi}_1$ and by $\underline{\pi}_2$ and $\underline{\pi}_3$, respectively. In text we discuss the contribution to the second derivative which results from the surface set $\underline{S}_i \cap \underline{\pi}_1$ and from the contour $\underline{\Gamma}_3$ lying upon $\underline{\pi}_3$. The infinitesimal surface element dS_i related to a generic point $P_i \equiv C_1$ is written as $dx\,dy$. C_3 is the perpendicular projection of C_1 upon $\underline{\pi}_3$. C_1H and C_3H are perpendicular to the edge AA'. The radius of the arc of circle $\underline{\Gamma}_1$ is r, while the distance C_1H_1 is denoted by x. Hence $C_1C_3 = x\sin\alpha$, $C_3H = x\cos\alpha$, and the radius of the arc of the circle $\underline{\Gamma}_3$ is given by $R_3(x) = (r^2 - x^2\sin^2\alpha)^{1/2}$. Finally, $\Phi_M(x) = x\hat{C}_3H_2 = \pi - H\hat{C}_3H_2$.

The last item is particularly important, because when r goes to zero, from Fig. 3 one can see that the limit of $\ddot{P}_{ij}(r)$ can depend on the way we let r approach zero. In fact, if we let the contour $\underline{\Gamma}_j$ shrink to zero by maintaining C_1 fixed, $\underline{\Gamma}_j$ will necessarily become the null set so that the resulting contribution to $\ddot{P}_{ij}(r)$ would be zero. On the other hand, we could let r go to zero and simultaneously let C_1 approach the edge in such a way that the resulting $\underline{\Gamma}_j(\bar{r}_i, r)$ will always be composed of the two relevant subsets $\underline{\Gamma}_2$ and $\underline{\Gamma}_3$. In this case, neither $\hat{\sigma}_j(P_2)$ nor $\hat{\sigma}_j(P_3)$ will approach $\hat{\sigma}_i$ as $r \to 0$. Hence, as $r \to 0$, $\phi_j(l)$, defined in Eq. (3.7), will not approach $\pi/2$, and therefore we must expect that result (3.8) will no longer be true. Although both limiting procedures require an interchange of limits, it will soon appear clear that the conditions required for the validity of the interchange related to the second procedure are much weaker than those required by the first one.

To this aim, let us write the contribution to $\ddot{P}_{ij}(r)$ due to the two half planes $\underline{\pi}_1$ and $\underline{\pi}_3$ by using the explicit parametrization of the boundary set $\underline{\pi}_i \cap \underline{S}_i$, which is visualized in Fig. 3,

$$\ddot{P}_{ij}^{(13)}(r) = -\frac{1}{4\pi V}\int_{-L}^{+L} dy\, p_{ij}^{(13)}(y, r), \tag{4.1}$$

where

$$p_{ij}^{(13)}(y, r) \equiv \frac{1}{r^2}\int_0^{r/\sin\alpha} dx \int_{\underline{\Gamma}_3(x,y,r)} dl\, \hat{\sigma}_i(l)\cdot\hat{\omega}(l) \times \cot\Phi_j(l). \tag{4.2}$$

The upper limit of the first integral in Eq. (4.2) represents the distance of the generic point $P_i \equiv (x, y)$ from the edge AA', beyond which the sphere $\underline{B}(C_1, r)$ no longer intersects $\underline{\pi}_3$. The definition of the angle α is evident from Fig. 3. However, it is not useless to remark here that the previous upper limit is r when we consider the contribution $\ddot{P}_{ij}^{(12)}(r)$ due to the half planes $\underline{\pi}_1$ and $\underline{\pi}_2$. In fact, the general recipe is this: The upper limit is $r/\sin\alpha$ or r according to whether the smallest of the two dihedral angles between the two considered half planes is smaller or larger than $\pi/2$. Correspondingly, in the two cases α is the smallest dihedral angle or its complement to π, and thus the condition $0 \leq \alpha \leq \pi/2$ is always true.

We can continue the previous discussion. Indeed, we claim that the correct procedure for evaluating the zero-distance limit of $\ddot{P}_{ij}(r)$ when a sharp edge is present is the following:

$$\lim_{r\to 0} \ddot{P}_{ij}^{(13)}(r) = -\frac{1}{4\pi V}\int_{-L}^{+L} dy \lim_{r\to 0} p_{ij}^{(13)}(y, r). \tag{4.3}$$

Equation (4.3) represents the exact definition of the expression "second limiting procedure" we have used before. It also appears clear that through Eq. (4.3) the limit $r \to 0$ is interchanged only with the integration with respect to y, while through the procedure followed for obtaining Eq. (3.8) the further interchange with the x integration was required also.

We must now show why the limiting procedure (4.3) is correct. From Fig. 3, it is evident that $p_{ij}^{(13)}(y, r)$ is certainly a continuous function when y and r range, respectively, in the two intervals $[-L+\delta, L+\delta]$, $[0, \delta]$, where δ is a positive number which can be taken arbitrary small. The existence of the limit of $p_{ij}^{(13)}$ as $r \to 0$, which will be proved in Appendix B, assures us that the limit interchange (4.3) holds true, except, possibly at the two small end-point sets. Since we can let the measure of these two sets approach zero, barring unlikely pathological behavior of $p_{ij}^{(13)}$ at the end points, one concludes that Eq. (4.3) holds true all over the considered edges.

In Appendix B, we have directly evaluated $p_{ij}^{(13)}(y, r)$ for the sample's configuration we are considering. The result is given by Eq. (B18) and turns out r independent; therefore

$$\lim_{r\to 0} p_{ij}^{(13)}(y, r) = \tfrac{2}{3}[1 - (\pi - \beta_{ij}^{13})\cot(\pi - \beta_{ij}^{13})], \tag{4.4}$$

where β_{ij}^{13} $(0 < \beta_{ij}^{13} < 2\pi)$ is one of the two dihedral angles between the half planes π_1 and π_3. A straight edge is formed by the intersection of two half planes that delimit, respectively, the ith and the jth phase; by substituting this last result into Eq. (4.3), we can conclude that this straight edge contributes to the $\ddot{P}_{ij}(r)$'s zero-length limit with the quantity:

$$\ddot{P}_{ij}^{(13)}(0^+) = -\frac{1}{6\pi V}\int_{-L}^{L} dy\,[1 - (\pi - \beta_{ij}^{13})\cot(\pi - \beta_{ij}^{13})]. \tag{4.5}$$

From the previous particular configuration, we can immediately proceed to much more general cases. In fact, when more edges are present, we must sum over all edge contributions. When more than two half planes meet along the same edge, indexed through the integer l, we must sum over all possible pairs of (ith, jth) phases delimiting half planes. If we number these pairs with the index k, we find that the zero-length limit of the second derivative of the stick-probability function is given by

$$\ddot{P}_{ij}(0^+) = -\frac{1}{6\pi V}\sum_l \int dy \sum_k \{1 - [\pi - \beta_{ij}^k(y)] \times \cot[\pi - \beta_{ij}^k(y)]\}, \tag{4.6}$$

where for notational simplicity we have not specified both the limits of the integrations and of the sum. So far, we have confined ourselves to the case of straight edges. However, with the case of curves one expects that Eq. (4.6) still holds true. In this case the relevant integral must be interpreted as a curvilinear one, and $\beta_{ij}^k(y)$ represents the dihedral angle between the half-planes which are tangent to the kth pair's separating surfaces at the point $P(y)$ which lies on the considered edge and which is characterized by the curvilinear abscissa y. An equivalent way for defining the angles $\beta_{ij}^k(y)$ is the following: Imagine that the considered lth edge at the point $P(y)$ is cut with a plane perpendicular to the edge.

This plane will cut the surfaces which are confluent on the edge along some lines. Choose the lines which correspond to the kth pair. $\beta_{ij}^k(y)$ is the angle between the tangents (more precisely the limits of the tangents) to these two curves at the point P.

From this discussion, it appears evident that the edges must be endowed with a tangent at any of their points and moreover that the separating surfaces must be C_2 functions except for the intersection edges. In this way we are sure that all quantities which appear in Eq. (4.6) exist. Moreover, these conditions should suffice for obtaining a rigorous proof of Eq. (4.6) according to the following argument. One locally approximates intersecting boundaries through wedges that meet. The previous continuity assumptions should assure us that the corresponding error is $O(r)$. Consequently the limit $r \to 0$ gives the result (4.6). Before concluding the paper, we want, however, to give two simple applications of result (4.6).

Let us first consider the simple two-phase system made of one cylinder, whose height and radius are h and R, respectively. The discontinuity lines are the two circles which delimit the two bases. Along these lines, the angles β_{12} are equal to $3\pi/2$. Then we get

$$\ddot{P}_{12}(0) = -\frac{1}{6\pi V}(2\pi R + 2\pi R)2\,,$$

where the factor 2 accounts for the fact that we have two pairs of intersecting half planes. Since the system is a two-phase one, from Eq. (3.7) we derive that $P_{12}(r) = -\ddot{P}_{11}(r)$. Hence $\ddot{P}_{11}(0) = 4R/3V$. This result coincides with the corresponding value calculated from the correlation function

$$P_{11}(r) = 1 - \frac{rS_t}{4V} + \frac{r^2 2R}{3V} + \frac{r^3}{64R^3} - \frac{r^4}{30\pi R^3 h}\,,$$

$$V \equiv \pi R^2 h, \quad S_t \equiv 2\pi R^2 + 2\pi R h\,,$$

relevant to this system and evaluated directly from Eq. (2.12) by Mering and Tchoubar [see Eq. (3.10) of Ref. 15].

As a second example, let us consider the case of a prism whose base is an equilateral triangle. Let the triangle's side be a, and the height of the prism be h. In order to evaluate $\ddot{P}_{12}(0)$, we apply Eq. (4.6) once more. Now, along the three vertical edges the angle β_{12} is $5\pi/3$, while along the six horizontal edges the relevant angle β_{12} is $3\pi/2$. Hence we get

$$-\ddot{P}_{11}(0) = \ddot{P}_{12}(0) = -\frac{1}{\pi V}\left(2a + h + \frac{2\pi h}{3\sqrt{3}}\right).$$

By direct evaluation we have found that, at small r, the correlation function relevant to the previous system is

$$P_{11}(r) = 1 - \frac{rS_t}{4V} + \frac{r^2}{6\pi V}\left(6a + 3h + 3h\,\frac{2\pi}{3\sqrt{3}}\right) - \left(\frac{2\pi}{3} + \sqrt{3}\right)\frac{\sqrt{3}}{16\pi V} r^3\,,$$

where S_t is the total surface. Thus one can immediately check that Eq. (4.6) gives the right result.

V. CONCLUDING REMARKS

Perhaps it is not fully useless to note that the expressions we have obtained for the first and second derivatives of the stick-probability functions—i.e., Eqs. (2.20), (3.1), and (3.7)—can be taken as correct even when the phase-delimiting surfaces do not share the continuity conditions we have required in working out the previous expressions. In fact, from a practical point of view, it seems sufficient to require the existence of the relevant integrals.

We have taken this attitude in evaluating the zero-length limits of the two previous quantities $\dot{P}_{ij}(0)$ and $\ddot{P}_{ij}(0)$. However, this analysis must be carefully done, owing to involved limit interchanges. We believe that through Eqs. (3.8) and (4.6) we have correctly analyzed the cases which are physically the most important ones. In particular, Eq. (4.6) takes into account the contributions of all singularities except for isolated singular points. However, at least for convex bodies, the last singularities, i.e., the vertices, should not contribute as is indicated by the known expression of P_{ij} for cubes, prisms, etc. Therefore one can believe that Eq. (4.6) has been proved with the same accuracy of the generalized formulations (2.20), (3.1), and (3.7).

Mathematically it is amusing to note that the stick-probability functions relevant to different

phases must always be convex and increasing r functions in a neighborhood of the origin. This follows from the fact that (a) $\dot{P}_{ij}(0)>0$ according to Eq. (2.21a) and (b) $\ddot{P}_{ij}(0^+)\leq 0$ according to Eq. (3.8) or (4.6). Indeed the integrand of Eq. (4.6) is a negative-valued function whose values range in the set $[0,-\infty]$, as the variable $\pi-\beta_{ij}^k$ ranges in the physically allowed set $[-\pi,\pi]$.

From a physical point of view, it must be emphasized that Eq. (4.6) might be very useful. In fact, when we can sensibly approximate the dihedral angles values, then Eq. (4.6) will give a direct correlation between the value $\ddot{\gamma}(0)$ and the specific length L/V, where L denotes the total length of the edges. Thus the experimental determination of the scattered intensity allows us to know $\ddot{\gamma}(0)$ and consequently the specific length also. The knowledge of the latter can be very important. Indeed, over the past years there has been a great deal of experimental evidence that different types of surface sites have different chemistries,[16] and thus the chemical behavior of edge atoms should be different from that of atoms lying inside the regular part of the surfaces. Now the edge specific length is proportional to the number of atoms which are located on the edges. Consequently, Eq. (4.6) allows us to exploit possible quantitative connections between the catalytic properties of a sample and the specific length of its edges.

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APPENDIX A: EVALUATION OF $\ddot{P}_{ij}(0^+)$ FOR CONTINUOUS BOUNDARIES

We must show that if the boundary surfaces are continuous differentiable functions, then the limit of the second derivative of $P_{ij}(r)$, as $r\to 0+$, is zero. More definitely, according to the discussion in Sec. III, we must show that at each point P_i of the boundary $\underline{S}_{ij}$ between the ith and the jth phase one has

$$\lim_{r\to 0}\oint_{\Gamma_j} dl\,\frac{\cot\phi_j(l)\hat{\sigma}_i\cdot\hat{n}}{r^2}=0. \tag{A1}$$

Clearly, the contour along which the integral is evaluated lies on the surface $\underline{S}_{ij}$ as well as on the sphere of radius r. For the last condition, the contour has a finite length unless it has an infinite number of "oscillations." However, this possibility is ruled out by the C_2-continuity properties of S_{ij}. Hence the contour for finite r's has a finite length and, consequently, the integral (A1) is evaluated on a compact set.

In order to analyze the behavior of remaining factors inside the integral (A1), let us refer to Fig. 4, where Σ and Σ' denote, respectively, the sections of the surface $\underline{S}_{ij}$ with the figure's plane and the circle which osculates Σ at P_i. There, $|P_iP|=r$, while $\hat{\omega}$ is parallel to P_iP, and $\hat{\sigma}_i\cdot\hat{\omega}=\cos\phi_i$.

It follows that $|PP'|=O(r)$, $|P_iP|=|P_iP'|+O(r)$, and $\hat{\omega}\cdot\hat{\omega}'=1+O(r)$. Moreover, the continuity conditions imply that $(\hat{\omega}\cdot\hat{\sigma}_j)\equiv\cos\phi_j=(\hat{\omega}'\cdot\hat{\sigma}')+O(r)$ and $\hat{\sigma}_i\cdot\hat{\omega}=\hat{\sigma}_i\cdot\hat{\omega}'+O(r)$. If we denote by R the radius of the osculating circle Σ', from the previous relation and from Fig. 3 one immediately sees that

$$\cos\Phi_i=(\hat{\sigma}_i\cdot\hat{\omega}')+O(r)=\frac{P_iP'}{2R}+O(r)=\frac{P_jP}{2R}+O(r)$$

and

$$\cos\phi_j=(\hat{\omega}\cdot\hat{\sigma}_j)=(\hat{\omega}'\cdot\hat{\sigma}')+O(r)$$
$$=\cos\phi_i+O(r)=\frac{r}{2R}+O(r).$$

By substituting these two last expressions in the integral (A1) one realizes that the limit as $r\to 0$ of the function which must be integrated is finite at any fixed P_i. But, as we have said before, the integral is performed on a compact set whose measure goes to zero as $r\to 0$. Hence Eq. (A1) is proved once we assumed that the limit interchange is correct.

APPENDIX B: EXISTENCE OF LIMIT OF p_{ij}^{13}

With reference to Fig. 3 we want to evaluate now the following integral:

$$p_{ij}^{(13)}(y,r)\equiv\frac{1}{r^2}\int_0^{r/\sin\alpha}dx\int_{\Gamma_3(x,y,r)}dl\,\Psi_{ij}(x,y,r) \tag{B1}$$

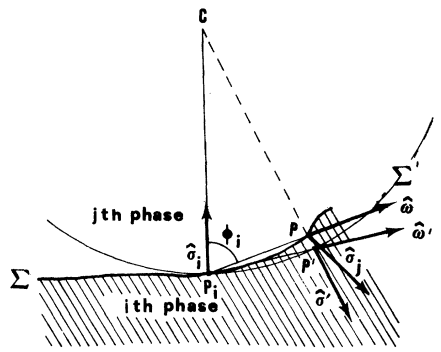

FIG. 4. Normal section of the separating surface $\underline{S}_{ij}$.

where we have set for convenience

$$\Psi_{ij}(x,y,r) \equiv \hat{\sigma}_i(l) \cdot \hat{\omega}(l) \cot\Phi_j(l) \tag{B2}$$

It is also convenient to split the integral (B1) into two contributions:

$$p_{ij}^{(13)}(y,r) = p_1(y,r) + p_2(y,r), \tag{B3}$$

where

$$p_1(y,r) \equiv \frac{1}{r^2} \int_0^r dx \int_{\Gamma_3(x,y,r)} dl\, \Psi_{ij}(x,y,r), \tag{B4}$$

and

$$p_2(y,r) \equiv \frac{1}{r^2} \int_r^{r/\sin\alpha} dx \int_{\Gamma_3(x,y,r)} \Psi_{ij}(x,y,r) dl. \tag{B5}$$

Since in the two cases, (B4) and (B5), the contour $\Gamma_3(x,y,r)$ is an arc of a circle or a complete circle, respectively, it is convenient to parametrize the second integration variable as well as the integrand in terms of the angle φ between the axis X' and the vector C_3P, where P is a generic point belonging to Γ_3 (see the caption of Fig. 3 for more details on the definition of some symbols). To this aim, we observe that

$$C_1P = C_1C_3 + C_3P = r\hat{\omega}(l), \tag{B6a}$$

$$C_1C_3 = -x\sin\alpha\hat{\sigma}_j, \quad \hat{\sigma}_i \cdot \hat{\sigma}_j = \cos\alpha. \tag{B6b}$$

Since the Cartesian components of C_3P with respect to $HX'Y'Z'$ are $(R_3(x)\cos\varphi, R_3(x)\sin\varphi, 0)$ where $R_3(x)$, the radius of $\Gamma_3(x,y,r)$, is given by

$$R_3(x) = (r^2 - x^2\sin\alpha)^{1/2}, \tag{B6c}$$

and the components of $\hat{\sigma}_i$ are $(-\sin\alpha, 0, \cos\alpha)$, then by using Eqs. (3.6a)–(3.6c) we immediately obtain

$$\hat{\sigma}_i \cdot \hat{\omega}(P) = [-x\sin\alpha\cos\alpha - R_3(x)\sin\alpha\cos\varphi]/r. \tag{B7}$$

From the relation

$$\cos\Phi_j(P) \equiv \hat{\sigma}_j(P) \cdot \hat{\omega}(P) = -x\sin\alpha/r \tag{B8a}$$

we get very easily that

$$\cot\Phi_j(P) = -x\sin\alpha/R_3(x). \tag{B8b}$$

Finally, the integrand becomes

$$\Psi_{ij}(x,y,r) = \frac{x^2\sin^2\alpha\cos\alpha}{rR_3(x)} + \frac{x\sin^2\alpha\cos\varphi}{r}. \tag{B9}$$

We can now start with the direct evaluation of integrals (B4) and (B5). In fact, Eq. (B5) can be written as

$$p_2(y,r) = \frac{1}{r} \int_r^{r/\sin\alpha} dx \int_{-\pi}^{\pi} R_3(x) d\varphi\, \Psi_{ij}(x,y,r),$$

and after using Eq. (B9) we have

$$p_2(y,r) = (2\pi/3)\sin^2\alpha\cos\alpha(1/\sin^3\alpha - 1). \tag{B10}$$

The evaluation of $p_1(y,r)$ is a little bit more involved, since the contour Γ_3 is an arc of a circle, whose corresponding angle is $2\Phi_M$ and

$$\Phi_M(x) = \pi - \arccos[x\cos\alpha/R_3(x)] \tag{B11}$$

(see Fig. 3). By using Eqs. (B11), (B9), and (B4), we have

$$p_1(y,r) = \frac{\sin^2\alpha\cos\alpha}{r^3} \int_0^r x^2 dx\, 2\phi_M(x) + \frac{2\sin^2\alpha}{r^3} \int_0^r R_3(x) x\, dx \sin\phi_M(x). \tag{B12}$$

Now, the calculation of the second integral is trivial and gives

$$\tfrac{2}{3}\sin^2\alpha \tag{B13a}$$

while the calculation of the first integral through the relation

$$\frac{2\sin^2\alpha\cos\alpha}{r^3}\left[\frac{\pi}{3}r^3 - \int_0^r x^2 dx \arccos\left(\frac{x\cos\alpha}{R_3(x)}\right)\right] \tag{B13b}$$

amounts to the calculation of the following integral:

$$\int_0^r x^2 dx \arccos\left(\frac{x\cos\alpha}{R_3(x)}\right). \tag{B14}$$

The last task can be accomplished by first performing an integration by parts and subsequently changing the variables $r^2 - x^2 \equiv z^2r^2$. In this way, after straightforward manipulations one finds that the value of (B14) is

$$(r^3/3)\cos\alpha[-1/\sin^2\alpha + \alpha/(\sin^3\alpha\cos\alpha)]. \tag{B15}$$

By collecting all results, we get

$$p_{ij}^{(13)}(y,r) = \tfrac{2}{3}(\pi - \alpha)\cot\alpha + \tfrac{2}{3}. \tag{B16}$$

It is important to note that this result depends neither on y nor on r, and moreover that it is a decreasing positive-valued function of α in the subset $[0, \pi/2]$. The value $\alpha = 0$ must be excluded, since at such a value the half plane π_3 is strictly coincident with π_1 and the decomposition (B3) is no longer true.

So far we have not considered all possible relative orientations of half planes π_1 and π_3. Indeed, result (B16) explicitly refers to the case where the lowest of two possible dihedral angles between

$\underline{\pi}_1$ and $\underline{\pi}_3$ is lower than $\pi/2$. Therefore we must still analyze the case where the previously defined angle is greater than $\pi/2$, or more precisely, belongs to the set $[\pi/2, \pi]$. In Fig. 3, this situation corresponds to considering half planes $\underline{\pi}_2$ and $\underline{\pi}_1$, for instance.

By proceeding along the same lines we followed before, one can easily show that in this case one has

$$p_{ij}^{(12)}(y,r) = \tfrac{2}{3} - \tfrac{2}{3}\,\alpha\cot\alpha\,, \tag{B17}$$

where α (denoted by α_{12} in Fig. 3) corresponds to the π-complementary angle of the smallest dihedral angle between $\underline{\pi}_1$ and $\underline{\pi}_2$.

Finally, both Eqs. (2.16) and (2.17) can be expressed through the single relation

$$p_{ij}^{(lm)} = \tfrac{2}{3} - (\pi - \beta_{lm})\cot(\pi - \beta_{lm})\,, \tag{B18}$$

where β_{lm} denotes one of the dihedral angles between the half planes, indexed for greater generality by l and m, which meet along the common edge considered.

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[1]Throughout the paper, we follow the convention of denoting a set and its measure by the same capital letter, which, however, will be underlined when it refers to the first case. For unit vectors we shall use small Greek letters with carets.

[2]For example, R. P. Feynman, *Lectures on Statistical Mechanics* (Benjamin, New York, 1972), Sec. 4.4.

[3]A. H. Narten and H. A. Levy, J. Chem. Phys. 55, 2263 (1971).

[4]P. Debye, H. R. Anderson, Jr., and H. Brumberger, J. Appl. Phys. 28, 679 (1957).

[5]G. Porod, Kolloid Z. 124, 83 (1951).

[6]A. Peterlin, Makromol. Chem. 87, 152 (1965).

[7]J. Goodisman and H. Brumberger, J. Appl. Crystallogr. 4, 347 (1971).

[8]J. Goodisman and H. Brumberger, J. Appl. Crystallogr. 12, 398 (1979).

[9]R. Kirste and G. Porod, Kolloid Z. Poly. 184, 1 (1962).

[10]In order to avoid any confusion, we recall that our P_{12} is equal to $\frac{1}{2}$ the probability for dissimilar ends: P_D introduced in Sec. 1 or Ref. 4.

[11]I. M. Guelfand and G. E. Chilov, *Les Distributions* (Dunod, Paris, 1962), Vol. 1, Chap. 3.

[12]We recall that a quantity X is $O(\Delta r)$ when $\lim_{\Delta r \to 0} (X/\Delta r) \to 0$.

[13]T. J. Willmore, *Introduction to Differential Geometry* (Oxford University, New York, 1969), Chaps. 1 and 2.

[14]In fact, from Fig. 2 one immediately realizes that $\hat{\nu} = \hat{\omega} \times \hat{\tau}$, $\hat{\tau}_1 = \hat{\sigma}_j \times \hat{\tau}$. Then $(\hat{\nu}_\tau \cdot \hat{\tau}_1) = (\hat{\omega} \times \hat{\tau}) \cdot (\hat{\sigma}_j \times \hat{\tau}) = \hat{\sigma}_j \cdot [\hat{\tau} \times (\hat{\omega} \times \hat{\tau})] = \hat{\sigma}_j \cdot [\hat{\omega}\,(\hat{\tau} \cdot \hat{\tau}) - \hat{\tau}(\hat{\omega} \cdot \hat{\tau})] = \hat{\sigma}_j \cdot \hat{\omega}$.

[15]J. Méring and D. Tchoubar, J. Appl. Crystallogr. 1, 153 (1968).

[16]G. A. Somorjai, Science 201, 489 (1978).