Perimeter-area laws for a random agglomeration of particles

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A remarkable connection is established between the "volume" of a random agglomerate and its "surface area." This connection, which is based on the method of functional differentiation, is illustrated using a prototype of nucleation and growth models. Several directions for further generalizations of this method are also indicated.

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The perimeter of a circle is the R derivative of its area πR^2, namely, $2\pi R$, and the surface area of a sphere is the R derivative of its volume $\frac{4}{3}\pi R^3$. Is there a similar connection between the "volume" and the "surface area" of a random agglomerate such as the one shown in Fig. 1? This paper addresses this question and shows that there is indeed such a connection. It is based on the functional derivative.

Random agglomeration of particles is encountered in a variety of nucleation and growth phenomena leading to the formation of new solid phases: compact, porous, or particulate. Porous and particulate material systems offer a large effective surface area per unit volume and hence find applications requiring large contact areas such as catalytic reactors, electrochemical power sources (e.g., batteries and fuel cells), and supercapacitors, to name a few. In all this, a measure of the exposed area is of much interest. We present here a simple description of this areal measure of a random agglomerate of particles and illustrate it with a prototypical nucleation and growth model.

For ease of presentation and without loss of generality, the two-dimensional (2D) version of the random agglomerate shall be employed and consequently the perimeter will be the quantity of interest. Figure 1 shows a section of the 2D random agglomerate consisting of disks of different radii (R_i) and randomly overlapping with one another. In the absence of overlap, the perimeter is trivially given by $2\pi\sum_i R_i$ (ignoring edge effects, which are important for finite systems). In the presence of overlap, the perimeter depends not only on the set of radii (R_i) but also on the relative placement of the disks and becomes a highly complex random set.

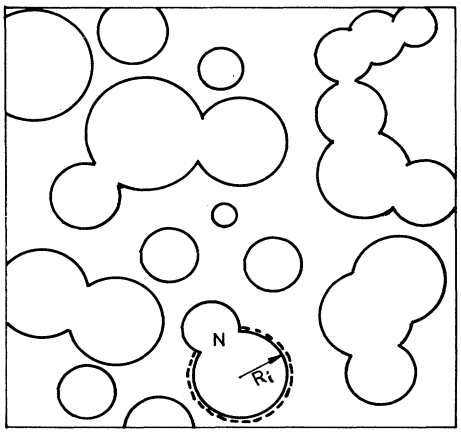

FIG. 1. 2D random agglomerate. The differential increase in the radius R_i of a cluster is indicated by dashed curve and N is the neck region.

The approach presented in this paper is essentially based on the simple observation that the perimeter $2\pi R$ of a circular disk is the rate of change of its area πR^2 with radius R. Extending this elementary principle to the overlapping disks in Fig. 1, it is realized that once we have somehow expressed the area S, covered by the disks, as a function of the disks' radii (R_i) and their placements (collectively denoted $\mathbb{P}$), the perimeter contributed by a particular radius R_i is simply given by [1]

$$L_i = \frac{\partial}{\partial R_i} S(R_1, R_2, \ldots, R_k; \mathbb{P}) \tag{1}$$

and the total perimeter

$$L = \sum_i L_i \ . \tag{2}$$

It must be appreciated at the outset that all complexities arising from the overlap scenario (including the overlap of the disks with the outer edges of a finite system) are buried in the function $S(R_1, R_2, \ldots, R_k; \mathbb{P})$.

Next, let the radii R_i range from zero to a maximum value of $\bar{R}$. Further, let this range of radius zero to $\bar{R}$ be parametrized by a continuous real variable ε such that ε ranges from a minimum value of ε_L to a maximum value of ε_U, within this range. Denote this parametrization by $R(\varepsilon)$. This parametrization device is useful in representing any given coverage function $S(R_1, R_2, \ldots, R_k; \mathbb{P})$ as $S(R(\varepsilon_1), R(\varepsilon_2), \ldots, R(\varepsilon_k); \mathbb{P})$. The perimeter L now takes the form

$$L = \sum_i \frac{\partial S}{\partial R_i} = \sum_i \frac{\partial S}{\partial R(\varepsilon_i)} = \int_{\varepsilon_L}^{\varepsilon_U} d\varepsilon \sum_i \delta(\varepsilon - \varepsilon_i) \frac{\partial S}{\partial R(\varepsilon_i)} \ . \tag{3}$$

The Dirac delta function $\delta(\varepsilon-\varepsilon_i)$ and the integration in Eq. (3) ensure that the summation with respect to i is only over those ε_i's that lie in the interval $[\varepsilon_L,\varepsilon_U]$. $(\varepsilon_1,\varepsilon_2,\ldots,\varepsilon_i,\ldots)$ can be viewed as a random series having several possible realizations. Now represent the Dirac delta function $\delta(\varepsilon-\varepsilon_i)$ as the *functional* derivative [2,3]

$$\frac{\delta R(\varepsilon_i)}{\delta R(\varepsilon)}=\delta(\varepsilon-\varepsilon_i)\ . \tag{4}$$

Equation (3) now becomes

$$L=\int_{\varepsilon_L}^{\varepsilon_U}d\varepsilon\sum_i\frac{\delta R(\varepsilon_i)}{\delta R(\varepsilon)}\frac{\partial S}{\partial R(\varepsilon_i)} \tag{5}$$

$$=\int_{\varepsilon_L}^{\varepsilon_U}d\varepsilon\frac{\delta S}{\delta R(\varepsilon)}\ , \tag{6}$$

where $\delta S/\delta R(\varepsilon)$ is the functional derivative of S with respect to the function $R(\ )$ at the point ε.

In general S is random and as is L. Randomness could enter S in several ways: coordinates of the centers of the disks and the total number of disks can all be random. Denoting by $\langle\ \rangle$ the average over these random variables, we have the following relationships between the statistical properties of S and L:

$$\langle L\rangle=\int_{\varepsilon_L}^{\varepsilon_U}d\varepsilon\frac{\delta\langle S\rangle}{\delta R(\varepsilon)}\ , \tag{7}$$

$$\langle L^2\rangle=\int_{\varepsilon_L}^{\varepsilon_U}\int_{\varepsilon_L}^{\varepsilon_U}d\varepsilon_1 d\varepsilon_2\frac{\delta^2\langle S(1)S(2)\rangle}{\delta R_1(\varepsilon_1)\delta R_2(\varepsilon_2)}\bigg|_{R_1(\ )=R_2(\ )=R(\ )} \tag{8}$$

and so on for higher moments.

A remark is in order on the units of $\langle L\rangle$ in Eq. (7). As it stands, the unit of $\langle L\rangle$ comes out as $(\text{length})^{-1}$. This is because $\langle S\rangle$ represents only the *fraction* of length (in one dimension), area (in two dimensions), or volume (in three dimensions) that is covered by the 1D, 2D, or 3D clusters, respectively and hence $\langle S\rangle$ as used is dimensionless. Hence $\langle S\rangle$ needs to be multiplied by the actual length, area, or volume of the system so that $\langle L\rangle$ and its analogs for one and three dimensions appear with their proper units.

Equations such as (6) and (7) provide a connection between the perimeter L and the corresponding area S; a functional differentiation over S followed by an integration yields L. Of course, in order for this connection to be useful, S or $\langle S\rangle$ must be known as a functional of $R(\ )$.

Quite extensive work is available on $\langle S\rangle$. We shall now briefly digress in order to describe it. Since this work refers to a certain class of nucleation and growth models, we shall first explain this model type and then proceed to summarize developments aimed at finding $\langle S\rangle$.

Consider a 2D domain of area A (cf. Fig. 1) in which disk-shaped clusters nucleate at random times $(\tau_1,\tau_2,\tau_3,\ldots)$ and grow from locations having a prescribed spatial distribution. Denoting by dR/dt the rate of radial growth of a cluster, the radius $R(t,\tau)$ at time t of a cluster that nucleated at time τ is clearly

$$\int_\tau^t\left[\frac{dR}{dt}\right]_y dy\ . \tag{9}$$

If the state of nucleation and growth of the system is observed at time t, several clusters having the following radii will be seen in any one realization:

$$(R(t,\tau_1),R(t,\tau_2),R(t,\tau_3),\ldots)\ . \tag{10}$$

For the random time series $(\tau_1,\tau_2,\tau_3,\ldots)$, a homogeneous Poisson process with a constant rate parameter λ_0 or, in general, a nonhomogeneous Poisson process with a time-dependent rate $\lambda(t)$ is usually assumed. For the spatial distribution of the clusters, two types of distributions have been used so far: (i) a uniform distribution and (ii) the Neyman-Scott cluster process [4.5]. Earlier work by Canac [6], Kolmogoroff [7], Avrami [8], and Evans [9] resulted in the equation [10] for $\langle S\rangle$

$$\langle S\rangle=1-\exp\left[-\pi\int_0^t\lambda(\tau)R^2(t,\tau)d\tau\right]\ . \tag{11}$$

This expression is appropriate for the case of a large system with a uniform spatial distribution of clusters and a Poisson distribution for the temporal part. More recently, Eq. (11) has been generalized, with the aid of Robbins's theorem [11], in two important directions: (i) a theory for small systems [5,12,13] and (ii) formulations that employ more general spatial processes [5,14], such as the Neyman-Scott cluster process. The relationship of the overlap problem to the nearest-neighbor statistics of the underlying point process has also been pointed out [15].

Returning now to our original perimeter problem and making use of Eqs. (7) and (11), we obtain the perimeter law

$$\frac{\delta\langle S\rangle}{\delta R(t,\varepsilon)}=\exp\left[-\pi\int_0^t\lambda(\tau)R^2(t,\tau)d\tau\right]2\pi\lambda(\varepsilon)R(t,\varepsilon) \tag{12}$$

and

$$\langle L\rangle=\exp\left[-\pi\int_0^t\lambda(\tau)R^2(t,\tau)d\tau\right]\times 2\pi\int_0^t\lambda(\varepsilon)R(t,\varepsilon)d\varepsilon\ . \tag{13}$$

Note that in Eqs. (12) and (13), the time t is treated as a fixed parameter.

Several interesting and special cases of Eq. (13) arise depending on the choice of the nucleation rate $\lambda(t)$ and the growth rate dR/dt, which may, in general, have arbitrary time dependences. A simple choice for the growth rate is $dR/dt=K$, a constant. Two special choices for the nucleation rate are

$$\lambda(t)=\lambda_0\ \ (\text{a constant nucleation rate})\ , \tag{14}$$

$$\lambda(t)=N_0\delta(t)\ \ (\text{instantaneous nucleation})\ . \tag{15}$$

The latter is called instantaneous nucleation since N_0 clusters nucleate (per unit area and on the average) simultaneously at zero time. In Eq. (15), $\delta(t)$ is the Dirac delta

TABLE I. Formulas for $\langle L \rangle$ and its analogs in one, two, and three dimensions. Two different nucleation rates and a constant growth rate are employed.

Dimension	Nucleation rate	$\langle L \rangle$ or its analogs
1	$N_0\delta(t)$	$2N_0\exp[-2N_0Kt]$
1	λ_0	$2\lambda_0 t\exp[-\lambda_0 Kt^2]$
2	$N_0\delta(t)$	$2\pi N_0 Kt\exp[-\pi N_0 K^2 t^2]$
2	λ_0	$\pi\lambda_0 Kt^2\exp[-\pi\lambda_0 K^2 t^3/3]$
3	$N_0\delta(t)$	$4\pi N_0 K^2 t^2\exp[-4\pi N_0 K^3 t^3/3]$
3	λ_0	$\frac{4}{3}\pi\lambda_0 K^2 t^3\exp\left[-\frac{\pi}{3}\lambda_0 K^3 t^4\right]$

function.

Explicit formulas are presented in Table I for $\langle L \rangle$ and its analogs in one and three dimension for the constant and the instantaneous nucleation rates [cf. Eqs. (14) and (15)]. Note that the appropriate units for $\lambda(t)$ are $L^{-1}T^{-1}$ (in one dimension), $L^{-2}T^{-1}$ (in two dimensions), and $L^{-3}T^{-1}$ (in three dimensions).

Two additional remarks on Eq. (13) are in order. First, for instantaneous nucleation, Eq. (13) reduces to

$$\langle L \rangle = \exp[-\pi N_0 R^2(t,0)]2\pi N_0 R(t,0) . \tag{16}$$

This is just the ordinary derivative of $\langle S \rangle$ with respect to $R(t,0)$. Second, for constant growth rate K, $\langle L \rangle$, as given by Eq. (13), is related to the time derivative of $\langle S \rangle$ as

$$\langle L \rangle = \frac{1}{K}\frac{d\langle S \rangle}{dt} . \tag{17}$$

However, for time-dependent growth rates, such a relation does not hold.

Independent of the mathematical description presented above, one could anticipate the following scenario for the time evolution of the perimeter. For small times, when overlap is negligible, the total perimeter increases as the disks grow in their radii. However, the overlap phenomenon, which progressively comes into effect, works in the opposite direction and may [16] eventually cause the perimeter to decline to zero. This is what is expected in two and three dimensions. Formulas in Table I for the two and three dimensions correctly give rise to this anticipated behavior. The case of one dimension is exceptional in that the point edges that now constitute the "perimeter" can never increase in number through growth of the linear segments, but they are only progressively annihilated by overlap. Hence, for one dimension and for instantaneous nucleation and constant growth rate, the perimeter

$$\langle L \rangle = 2N_0\exp[-2N_0Kt] \tag{18}$$

falls monotonically in time. Of course, for a constant nucleation rate, new point edges are being constantly created, which, in combination with overlap, lead to a behavior similar to that of two and three dimensions (see Table I).

To conclude, a simple connection is established between an n-dimensional random agglomerate volume and its $(n-1)$-dimensional boundary area. This connection is valid irrespective of such complexities, which may go into the construction of the n-dimensional volume $\langle S \rangle$, as finite system geometries and more general spatial and temporal distributions of the underlying process. The growth function $R(t,\varepsilon)$ could also be stochastic, in which case an additional averaging needs to be performed over and above the space-time overaging implied by $\langle\ \rangle$ for the nucleation process. Higher moments of the perimeter such as $\langle L^2 \rangle$ can also be computed once the higher-order correlations of the coverage such as $\langle S(1)S(2) \rangle$ become available. An appropriate *functional* generalization of the Robbins theorem may provide these correlations.

One may further generalize this formalism to noncircular and nonspherical geometries. To be specific, consider a noncircular object prescribed by its support function $p(\phi)$ [to be distinguished from the radial distance function $r(\theta)$] in two dimensions. Our random agglomeration problem now acquires an additional random variable because the spatial orientation Θ of the noncircular object (relative to a fixed axis) can also be random, having a distribution $\rho(\Theta)$ [17]. A generalization is available [18] for finding $\langle S \rangle$ in this case too; however, for large systems, where edge effects are unimportant, $\langle S \rangle$ turns out to be independent of $\rho(\Theta)$ and is given by

$$\langle S \rangle = 1-\exp\left[-\int_0^t \lambda(\tau)A(t,\tau)d\tau\right] , \tag{19}$$

where

$$A(t,\tau) = \tfrac{1}{2}\int_0^{2\pi}\{p^2(\phi)-[p'(\phi)]^2\}d\phi \tag{20}$$

and the support function $p(\phi)$ is time dependent. Now a formula for $\langle L \rangle$ can be found as follows. The area A of the noncircular object

$$A = \tfrac{1}{2}\int_0^{2\pi}[p^2-(p')^2]d\phi \tag{21}$$

is connected to its perimeter

$$\int_0^{2\pi} p\,d\phi$$

through the equation [19]

$$\int_0^{2\pi} d\xi\frac{\delta A}{\delta p(\xi)} = \int_0^{2\pi} p\,d\phi . \tag{22}$$

Using this generalized connection between area and perimeter, Eq. (6) is generalized to

$$L = \int_{\varepsilon_L}^{\varepsilon_U} d\varepsilon\int_0^{2\pi} d\xi\frac{\delta S}{\delta p(\xi,\varepsilon)} , \tag{23}$$

where ε and ξ correspond, respectively, to the time and angular dependences.

There are also nucleation and growth problems of "mixed dimensionality," e.g., 3D nuclei, say, hemispherical, pinned to a 2D substrate [20]. Pinning destroys the

randomness required for applying formulas such as Eq. (11). Nonetheless, formulas are available [20] to treat these cases too, from which the corresponding formulas for the perimeter or its analogs could be reached.

Though, in this paper, we have considered only the first functional derivative of the n-dimensional volume S, it is interesting to ask what $(n-2)$-dimensional object the second functional derivative of S corresponds to. An upper bound based on the second functional derivative is available [21] for the random set consisting of the points of intersections of the clusters, i.e., the neck regions (cf. Fig. 1).

It was not the intent of this article to develop the proposed "functional derivative principle" in all its generalities. However, we have indicated several directions for further work. It is also hoped that this principle, if properly adapted and/or generalized, could find applications wider than the ones described here.

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[1] It should be noted here that contributions to the differential increment δS from the neck regions (see Fig. 1) require careful consideration. However, such contributions are of second order in δR_i and hence do not affect the first derivative of S in Eq. (1).
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