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Some surface effects in porous fractals

F. Brochard

Laboratoire de Physique de la Matière Condensée (*), Collège de France, 11 place Marcelin Berthelot, 75231 Paris Cedex 05, France

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Abstract. — Certain porous media have been claimed to be fractals in a broad range of scales $a < l < L$. The fractal dimension $D_f$ of the solid/void interface influences various surface effects characterized by a penetration length $l_s$. If $l_s$ can be varied (by suitable external agents) through the interval $(a, L)$, some information on $D_f$ can be extracted. We construct a tentative list of static physical processes leading to a variable $l_s$: a) adsorption of latex spheres (of radii $R = l_s$); b) depletion layers in a polymer solution, where the polymer is repelled by the wall, with specific implications for gel permeation chromatography; c) grafting of chains, in the (usual) regime where the grafting reaction stops whenever neighbouring chains begin to overlap; d) preferential adsorption of one species in a binary mixture near criticality. Whenever the fractal dimension of the critical clusters $D_c (\sim 2.5)$ is larger than $D_f$, the excess adsorption is controlled by the correlation length $\xi (= l_s)$ and diverges near the critical point.

1. Surface fractals.

Porous media with high specific areas play an important role in many fields: hydrology, oil sciences, oil technology, heterogeneous catalysis, chromatography, electrochemistry and so on. Sometimes the high area systems have a relatively narrow distribution of pore sizes (say, over less than a decade). In certain other cases, the distribution of pore sizes is extremely broad (say, over three decades or more). Certain porous media of the second group can be described as fractals in a certain range of lengths $a \leq l \leq L$. This means that they are statistically self-similar, or, in more concrete terms, that it is not possible to discriminate between two photographs of the same medium taken with two very different frame sizes ($l_1, l_2$) (with $l_1 > l_2$ in the fractal interval $(a, L)$).

It often happens that the upper limit $L$ is the size of the grains out of which the macroscopic structure is built. The lower limit $a$ may be as small as a molecular size.

Various experiments suggest the possible existence of fractal structures in certain porous media, e.g. sandstones [1], industrial aluminas or silicas [2-3], or coals [4]. Some of these experiments will be reviewed later in this section after a brief reminder of the fractal dimension $D_f$.

1.1 Definition of $D_f$. — $D_f$ is the fractal dimension of the interface ($2 < D_f < 3$). $D_f$ can be defined in the following way. We generate spheres of radius $\varepsilon$ with their centres around every point of the interface of one grain (size $L$). The volume spanned by the spheres per grain is

$$\Omega(\varepsilon) = L^{D_f} \varepsilon^{d-D_f}$$

(1)

(*) Unité Associée au C.N.R.S. n° 792 (U.A. 792).
where \( d = 3 \) is the space dimension. For many qualitative purposes, we may present this differently. Instead of using a continuum of spheres, we can restrict our attention to a discrete set of spheres in contact with each other \(- (L/\varepsilon)^{D_f} \) is then the number of spheres. A related qualitative picture, used in reference [2], is the following. The interface is covered with *tiles* of size \( \varepsilon \). The surface \( \Sigma(\varepsilon) \) covered by the tiles depends on their size: large tiles cannot follow the details of the irregular surface. Then

\[
\Sigma(\varepsilon) = L^{D_f} \varepsilon^{(d-1)-D_f} = \frac{\Omega(\varepsilon)}{\varepsilon}.
\]

We discuss the limitations of this tiling process in section 2.1.

1.2 Evidence for fractal porous structure.

1.2.1 Small scales (1 Å \( \leq r \leq 100 \) Å). — Adsorption data for small molecules on silica absorbers have been interpreted by Pfeifer and Avnir [2] in terms of the size \( r \) of the absorbed molecules. The number \( n \) of molecules absorbed per unit volume decreases as

\[
n \sim r^{-D_f} \quad (D \sim 2.7)
\]

They interpret \( D \) as the fractal dimension of the interface. Indeed, according to equation (2), if the molecules pack densely on the solid, the number of molecules \( n_g \) adsorbed per grain is

\[
n_g = nL^3 = \frac{\Sigma(r)}{r^D} = \left( \frac{L}{r} \right)^{D_f} \sim r^{-D_f}.
\]

Some criticism can be raised, however. First, \( r \) was varied only by a factor of ten. Second, the molecules were not chemically identical.

To cover a larger length range, and to use chemical analogues, the same group later reinterpreted some data on polystyrene adsorbed from a solvent on porous alumina [3]. They found the same law (Eq. (2)) by taking the radius of gyration \( R_g \) of the free polymer chains for \( r \).

In fact, a polymer chain is also a fractal. If \( N \) is the number of monomers, \( N \sim R_g^{D_p} \), with \( D_p = 5/3 \) in good solvent, \( D_p = 2 \) in \( \theta \)-solvent and \( D_p = 3 \) in bad solvent. The equilibrium adsorption of flexible polymers on a fractal surface has been discussed theoretically in reference [7]. The result is that \( n_g \) is independent of \( R_g \) as soon as \( D_p < D_f \). The interpretation of the adsorption data for PS is thus not obvious. They may well be dominated by kinetic effects: chains of size \( R_g \) cannot crawl into pores smaller than \( R_g \), although they would lower their free energy by increasing their number of contacts with the pore.

1.2.2 Intermediate scales (10 Å \( \leq r \leq 1000 \) Å). — Small angle X-ray or neutron scattering data [4] from lignite coal were interpreted by Bale and Schmidt in terms of the fractal dimension of the pore surface. Witten [5] gives a simple derivation of this result. One fills the space with spheres of size \( q^{-1} \); the spheres are either empty, partially empty or completely full. The scattering, due to density fluctuations, is entirely due to spheres which are partially full. The number of such spheres per grain is, according to equation (1),

\[
n_g(q^{-1}) = \Omega(q^{-1}) q^D = (Lq)^{D_f}.
\]

The data give \( D_f \approx 2.56 \pm 0.03 \) for lignite.

1.2.3 Large scales (10 Å \( \leq r \leq 100 \mu m \)). — A number of sandstones have been studied by Katz and Thomson [1]. They analysed sections of the rocks by electronic (SEM) or optical microscopy. They claimed that the rock is fractal over five decades of sizes (extending from 10 Å to 100 μm, the size of the sandgrains). \( D_f \) varies slightly from sample to sample (2.57 \( \leq D_f \leq 2.87 \)).

1.3 Physical processes which are sensitive to \( D_f \). — Whenever a physical process (near the surface) depends on an adjustable characteristic length \( l_s \), this process may allow probing of the fractal interface with a variable yardstick \( l_r \). However, in many instances, the measurements will be sensitive to various features of the surface, not only to \( D_f \). Here we shall discuss certain statistical and dynamical measurements which should be mainly sensitive to \( D_f \). A known example is diffusion controlled chemical reactions. Excitation transfer in fractal pores has been studied theoretically in reference [6]. The porous solid is saturated with a fluid which contains an excitable solute (a fluorescent or a phosphorescent dye) or a molecule which can react with active sites distributed on the interface. The molecules (excited at time \( t = 0 \)) diffuse toward the solid walls, where they are immediately relaxed. The relaxed molecules at time \( t \) are the molecules which are at a distance \( l_r = \sqrt{D Dt} \) of the interface, where \( D \) is the molecular diffusion coefficient in the fluid phase. If \( n(t) \) is the total number of excitable solute at time \( t \), we expect

\[
\frac{n(0) - n(t)}{n_0} = \frac{\Sigma(l_r) l_r}{L^3 P} = \frac{L^{D_f} (D t)^{3-D_f}}{L^3 P}
\]

where \( P \) is the porosity. The signal at small time is directly related to \( D_f \). This method is very flexible. Instead of operating with a time delay \( t \), one can operate with a modulated signal of frequency \( \Omega \), and the length scale is then \( \sqrt{D / \Omega} \): it can be varied over many decades.

We do not know of any experiment corresponding exactly to this proposal. Impedometric studies of porous electrodes have been carried out by Le Mélau.
télé [7] and interpreted by him in terms of a fractal geometry, but he insists that his basic process is not diffusion. What is the basic process in his experiments is still a mystery.

In a theoretical paper [16], de Gennes studied the partial filling of a fractal porous rock by a wetting fluid. He found that for certain simple examples the volume fraction of the liquid is given by \( \phi = P(L/r)^{3-D} \), where \( r \) is the Kelvin diameter for pore invasion and depends on the local vapour pressure. He points out, however, that the situation is complicated by many hysteretic effects.

Our aim in the present paper is to build up a list of relatively simple physical effects which can detect fractality.

2. Determination of \( D_f \) by adsorption of large objects.

2.1 Coating with latex spheres (Fig. 1). — It is possible to prepare latex particles of controlled size between 100 Å [8] and a few microns [9]. The latex suspension is stabilized by two possible means: a) electric charges (in water), and b) steric repulsion obtained by covering the latex with a copolymer PS/B, where B is a polymer which is not miscible with PS but is well soluble in the chosen solvent. The porous solid is incubated with the latex suspension. For case a), the sign of the latex charges must be opposite to the sign of the surface charges to provide attraction. We also want the superficial charge density of the latex to be smaller (or at least comparable) in absolute value than the charge density of the solid surface. In this way, the repulsion between adsorbed spheres is weak when compared to the attraction toward the solid, and we expect a good coverage of the interface. For case b), we must choose a polymer B which is strongly attracted by the interface.

The number of latex spheres of size \( b \) attached per grain is then \( n = (L/R)^{D_f} \). The quantity adsorbed per unit volume will be

\[
C_B = \left( \frac{L}{R} \right)^{D_f} \rho_B \frac{R^3}{L^3} = \left( \frac{L}{R} \right)^{D_f - 3} \rho_B .
\]

One must wash the porous solid with pure solvent to eliminate all free latex particles. Then one can either measure a density or an UV absorbance (in the UV band of PS). It may also be possible to use various diffraction methods (neutrons, X-rays or light scattering). The scattering intensity can be easily derived following reference [5]. We cover the interface with « coherent » spheres of size \( q^{-1} \). The number of spheres per grain is \( n_q = (Lq)^{D_f} \). The number \( n \) of latex spheres per sphere \( (q^{-1}) \), assuming \( qR < 1 \), is

\[
n = \frac{\Sigma(R)}{\Sigma(q^{-1})} \frac{1}{q^2 R^2} = \left( \frac{1}{qR} \right)^{D_f} .
\]

The structure factor \( S(q) \) is then

\[
S(q) = N_q \left( n \frac{R^3}{a^3} \right)^{D_f} = \left( \frac{L}{qa^2} \right)^{D_f} \left( \frac{R}{a} \right)^{6-2D_f} .
\]

The scattering experiment gives two ways to determine \( D_f \) : varying \( R \) and varying \( q \).

Critique of the tiling ansatz. — The basic ansatz of reference [2] is that if we adsorb objects (such as the latex spheres) with one and only one characteristic size \( R \), the number of objects adsorbed varies automatically as \( (L/R)^{D_f} \). This has been criticized on two geometrical grounds: accessibility and nesting.

(i) Fractals with low accessibility. It is mathematically possible to generate fractal objects in which the wiggly surface is inside a closed pore (no external aperture): of course, a surface of this type cannot be probed by adsorption studies.

A slightly less trivial case is obtained when the wiggly surface is in a nearly closed pore, but now this pore has a number of apertures of size \( b \). Three cases are compatible with self-similarity:

- \( b \) is small (of order \( a \)) for all pores,
- \( b \) is large (of order \( L \)) for all pores,
- \( b \) has a statistical distribution ranging from \( L \) to \( a \).

The latex spheres cannot probe the wiggly surface in the first situation \( (b \sim a) \), but they may do so in the two other cases. At the moment, we cannot think of a practical process (leaching, for example) which
would lead to \( b \sim a \) systematically, but one may be discovered in the future.

(ii) Fractals with nesting difficulties. When \( D_f \) is large, it may become difficult to nest a latex sphere which is tangent to the surface at one point \( M \) without having the sphere intersecting some other portion of the surface. A simple example (in 2 dimensions) is obtained if we take an ideal Gaussian chain with \( N \) freely jointed segments of length \( a \) as the fractal line. The r.m.s. size of this coil is \( Na^2 \), and the density of points is \( N/Na^2 \sim a^{-2} \) independent of \( N \). Here \( D_f = 2 \), but the area of the available holes between adjacent portions of the line is \( \sim a^2 \). Thus we cannot nest any « latex disk » of size \( R > a \) in such a structure. Effects of this type have been discussed recently by Van Damme (1). However, it is important to observe that certain fractal surfaces with large \( D_f \) (say \( D_f > 2.5 \)) can be compatible with the tiling ansatz for instance, the Menger sponge (\( D_f = 2.72 \)) discussed in reference [17].

2.2 Adsorbed polymer chains (Fig. 2). — This case is studied in details in reference [10]. For polymer adsorbed by a planar surface, de Gennes pointed out that the profile is self-similar and given by the simple law

\[
\xi(C) = r
\]

(11)

where \( \xi(C) \sim C^{-3/4} \) is the semi-dilute correlation length for a polymer solution at concentration \( C \).

The law (11) can be written as

\[
a^3 C(r) \sim \left( \frac{a}{r} \right)^{3-D_c} \quad r < R_G
\]

\[
C(r) \sim 0 \quad r > R_G
\]

where \( D_c \) is the fractal dimension of the coils \( D_c = \frac{5}{3} \) in good solvent and \( R_G \) the main radius of gyration. The concentration profile has been well confirmed experimentally [11].

The total number of adsorbed monomers per grain in full equilibrium is

\[
n_{\text{mono}} = \int_0^{R_G} C(r) \Sigma(r) \, dr.
\]

(13)

Inserting equation (11) gives

\[
n_{\text{mono}} = \left( \frac{L}{a} \right)^{D_f} \int_0^{R_G} \frac{dr}{r} \left( \frac{a}{r} \right)^{D_c-D_f}
\]

(14)

The integral is dominated by the small length limit and

\[
n_{\text{mono}} = \left( \frac{L}{a} \right)^{D_f}. \quad \text{The polymer forms a monolayer of size } a, \text{ independent of the degree of polymerization } N.
\]

The probe size is just a monomer size \( (l = a) \) ! This is due to the fact that polymer chains are not compact and adjust easily to surface heterogeneity.

However, experimental data to show a dependence upon \( N \). It is possible that equilibrium times are exceedingly long. The chains are first adsorbed as spheres of size \( R_G \), and it takes a long time for them to creep and fill the small structures. This leads to

\[
n = \left( \frac{L}{R_G} \right)^{D_f} N = \left( \frac{L}{a} \right)^{D_f} R_G^{3-D_f}
\]

(15a)

in better agreement with experimental data [3].

Experimental observation. — By density measurements, after washing and evaporating the solvent, one expects a density increase equal to

\[
d = \left( \frac{L}{a} \right)^{D_f} \frac{\Phi_p a^3}{P \rho_s L^2}
\]

(14b)

independent of \( N \) at equilibrium. However, if the chains behave as spheres of size \( R_G \), equation (15) leads to a reduction of \( C_e \):

\[
d' = d \left( \frac{R_G}{a} \right)^{5/3-D_f}
\]

(15b)

By neutron scattering, the two situations are interesting. For the fractal solid embedded by a polymer sheet of thickness \( a \), one expects from equation (10) with \( R = a \) that

\[
S_e(q) = L^{D_f} q^{-D_f}
\]

(16)
For the non-equilibrium case, equation (15),

\[ S(q) = S_0(q) \left( \frac{R}{a} \right)^{2(5/3 - D_r)} \]  

(17)

the scattered intensity is strongly reduced.

### 2.3 POLYMER DEPLETION AT THE SOLID/SOLVENT INTERFACE: APPLICATION TO GEL PERMEATION CHROMATOGRAPHY (G.P.C.) (Fig. 3).

With a suitable choice of solvent and surface treatment, the polymer is repelled by the interface and a depletion layer is expected to build up [12]. The thickness of the depletion layer is \( R_D \) — the chain radius of gyration — for a dilute solution and \( \xi(C) \) — the P-correlation length — for a semi-dilute solution. Thus, repulsive surfaces allow no to probe the interface with a variable yardstick \( 4(4 = R_G, C = C*, Is = C > C*) \).

If the porous solid is saturated with a polymer solution, the volume fraction occupied by the chains will be

\[ \frac{V}{PL^3} = 1 - \frac{\Omega(C)}{L^3} \]  

(18)

\( l_\xi = R_G, C < C^* \)

\( l_\xi = \xi, C > C^* \).

The concentration \( C_i \) per unit volume of the porous solid is then

\[ C_i = C_2 P \left[ 1 - \frac{\Omega(C)}{L^3} \right] \]  

(19)

This repulsive case is theoretically clean, but the difference \( \delta = \frac{C_1}{C_2} - 1 \) is small and hard to detect \( (\delta \sim (\xi/L)^{3-D_r} \sim 1/50) \). As pointed out to us by H. Benoit [15], G.C.P. leads directly to \( V \) (Eq. (18)).

### 2.4 GEL PERMEATION CHROMATOGRAPHY.

G.P.C. is a method of separating molecules by size. The separation is carried out on columns packed with a porous material. Large molecules, which are excluded from the pores, are eluted first. If the wall is repulsive, a species is eluted at a volume exactly equal to the volume available to it in the column. For very large molecules, the elution volume \( V_e \) is equal to the interstitial volume \( V_0 \). For very small molecules, \( V_e = V_0 + V_i \), where \( V_i \) is the internal pore volume. For intermediate size molecules, \( V_e = V_0 + K_d V_i \), where \( K_d \) is the partition coefficient. \( K_d \) is equal to the ratio of accessible pore volume to \( V_i \).

We estimate \( K_d \) for a column packed with a porous fractal material. In our notation, \( V_i = PL^3 \), and from equation (18)

\[ K_d = \left[ 1 - \frac{\Omega(R)}{3} \right] = 1 - \left( \frac{R}{L} \right)^{3-D_r} \]  

(20)

For \( R > L \), \( K_d \) is exponentially small.

\( R \) can be deduced from intrinsic viscosity measurements, and \( K_d \) is a simple way to derive \( D_r \).

**Remark:** It has to be noticed that nesting difficulties do not appear in the case of polymer depletion. On the other hand, the diameter of the pores must be of the order of \( l_\xi \) or \( L \) to be accessible to polymer chains.

### 2.5 GRAFTED POLYMER CHAINS.

Let us estimate the number of polymer chains (of polymerization index \( N \)) grafted on a porous solid (e.g. after silanization of the interface). Our basic assumption (following a current statement of the literature) is that a grafted chain excludes other chains [18]. The number of grafted chains will be, per grain,

\[ n = \left( \frac{R}{R_G} \right)^{D_r} \]  

(21)

or, in concentration of monomers per unit volume,

\[ \phi = \left( \frac{L}{R_G} \right)^{D_r - N} \]  

(22)

The number of grafted chains can be measured, after evaporating the solvent, through the difference of the weights at ambient \( T \) (with grafted chains) and at high temperature (where the grafted chains are decomposed and eliminated). Repeating the operation for different \( N \) values, we could, on principle, measure \( D_r \).

### 3. Determination of \( D_r \) with a binary critical mixture

#### 3.1 CRITICAL ADSORPTION.

In contact with a solid wall, a binary mixture has a concentration \( C_s \) at the wall different from the bulk concentration \( C \). If the mixture is near critical, this modification
is not restricted to the interface, but it extends over a length

$$\xi(T) = \xi_0 t^{-\nu}, \quad t = \frac{|\Delta T|}{T_c}$$

(23)

$$\xi_0 \sim 1 \text{ Å}$$ for small molecules and $$\xi_0 \sim 100 \text{ Å}$$ for polymer/solvent mixtures. The profile near the wall is discussed in reference [14]. At scales $$r < \xi$$, the profile becomes independent of $$t$$. In this critical region, it is useful to introduce a correlation length which depends only on concentration

$$\xi(T, C) = \xi_0 r^{-\nu} \left( \frac{\Delta C}{\Delta C_0} \right)^{-\nu/\beta} \approx \xi_0 \Delta C^{-\nu/\beta}$$

(24)

where $$\Delta C = C - C_\text{c}$$ is the difference between the concentration $$C(r)$$ near the wall and the critical concentration $$C_\text{c} - \Delta C_0 = l_0$$ is the order parameter below $$T_c$$

$$\xi(C) = \xi_0 \Delta C^{-\nu/\beta} = r$$

(25)

i.e.

$$a^\nu \Delta C(r) = \left( \frac{a}{r} \right)^{\nu/\beta} = \left( \frac{a}{r} \right)^{1 - D_B}$$

(26)

where $$D_B = d - \frac{2}{\nu}$$ is the Fisher exponent associated with the correlation function: $$\eta \approx 0$$ for $$d = 3$$ and $$\eta \approx 1/4$$ for $$d = 2$$. $$D_B$$ is the fractal dimension of a concentration fluctuation (or «cluster») ($$D_B \approx 2.5$$ for $$d = 3$$).

From equation (26), one can derive the increase of $$A$$ molecules near the interface

$$n_A = \left( \frac{L}{a} \right)^{D_B} \int_a^\infty \frac{r^{D_B}}{r^2} \left( \frac{a}{r} \right)^{3 - D_B} dr$$

(27)

a) $$D_B > D$$: the integral is dominated by the limit $$r = a$$:

$$n_A = \left( \frac{L}{a} \right)^{D_B}$$

(28)

$$l_s = a$$ and we expect no critical adsorption.

b) $$D_B < D$$: $$n_A$$ is dominated by the limit $$r = \xi$$:

$$n_A = \left( \frac{L}{\xi} \right)^{D_B} \left( \frac{\xi(T)}{a} \right)^{D_B - D}$$

(29)

which can also be written as

$$n_A = \left( \frac{L}{\xi} \right)^{D_B} \Delta C(\xi) \xi^3$$.

(30)

**Interpretation**: The concentration fluctuations or «clusters» are fractal objects, like polymer chains, with a fractal dimension $$D_B \approx 2.5$$ for $$d = 2$$.

— If $$D_B > D$$, the clusters are more irregular and can penetrate the smaller pores: the dominant clusters are then comparable in size to the lower cutoff ($$a$$).

Thus, experimental measurements might discriminate between fractals of dimensionality smaller or larger than $$D_B \approx 2.5$$. Moreover, these clusters are «ghost transient objects» which are able to enter pores of small apertures and for which nesting difficulties do not appear.

**Remark**: For $$d = 2$$ (for instance, demixtion of A/B lipids or liquid gas transition of a solute deposited on a surface and adsorbed on a protein or a polymer),

$$n_A = (L/a)^D \left( \frac{\xi(T)}{a} \right)^{2 - \frac{D}{3}}$$

where $$1 < D < 2$$ is the fractal dimension of the interface. Chromophores on the P-coil are sensitive to local environment. This may lead to a derivation of $$n_A$$.

**3.2 EXPERIMENTAL TECHNIQUES.**

**3.2.1 Density measurements.** — The change of density is given by $$\Delta d = n_A (d_A - d_B) (a/L)^3$$, i.e.

$$\Delta d = (d_A - d_B) \left( \frac{a}{L} \right)^{3 - D_B} \left( \frac{\xi(T)}{a} \right)^{D_B - D}$$

(31)

These variations of density are quite small. Typically taking $$a = 10 \text{ Å}$$, $$L = 1 \mu$$, $$\xi(T) = 1000 \text{ Å}$$, and $$D_B = 2.25$$, we get $$\Delta d / (d_A - d_B) \approx 3 \times 10^{-2}$$. One also needs a good equilibration of the concentration inside the grains. The diffusion coefficient of the binary mixture is $$D \sim kT/\eta$$ (where $$\eta$$ is the viscosity), and it is small in critical conditions. This means that we need independent grains of small size ($$L \approx 0.1 \text{ mm}$$) to allow for good equilibration.

**4.2 FLUORESCENT PROBES.** — One could use passive fluorescent probes, which are quenched in the bulk but less quenched in the adsorbed layer. A better trick may be based on the fact that the wavelength of the emitted light is very sensitive to the ambient polarity. Suitable chromophores in the A-rich region and in the B-rich region may send signals at different wavelengths. By using a filter to switch off the signals from the bulk, it may be possible to detect only the chromophores adsorbed at the interface.

**5. Conclusion.**

We have listed several physical means of investigating the fractal dimension $$D_B$$ of a porous solid. In all cases,
we absorb on a surface fractal a volume fractal of fractal dimension $D$ and size $l_s$. If $D > D_f$, the surface is graved with tiles of size $l_s$ and one measures $\Sigma(l_s)$. On the other hand, if $D < D_f$, one measures only $\Sigma(a)$. We give new predictions in the case of depletion layers and preferential adsorption of a binary mixture near criticality. We think that these two techniques, not yet discussed in the literature, will lead to a clean and accurate derivation of $D_f$.

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