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# Hydrodynamic Properties of Aggregates with Complex Structure

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## 1. Introduction

Hydrodynamic properties of fractal aggregates and polymer coils, such as sedimentation velocity, permeability, translational and rotational diffusion coefficients and intrinsic viscosity, are of great interest in hydrodynamics, engineering, colloid and polymer science and biophysics. The hydrodynamic properties of aggregates are closely connected to their structure.

Aggregates - the clusters of monomers - usually have a fractal structure which means that parts of the object are similar to the whole. The self-similar structure is characterized by the fractal dimension which is a measure of how the aggregate fills the space it occupies. The fractal dimension can be calculated by analyzing the mass-radius relation for a series of similar aggregates, since the mass of an aggregate scales as a power of the size.

The fractal dimension can be also determined by covering the aggregate with spheres of changing radius (Fig. 1). Then plotting the number of spheres  $N(\rho)$  versus their radius  $\rho$  in a log-log coordinate system, one determines the fractal dimension as the negative slope of the obtained line.

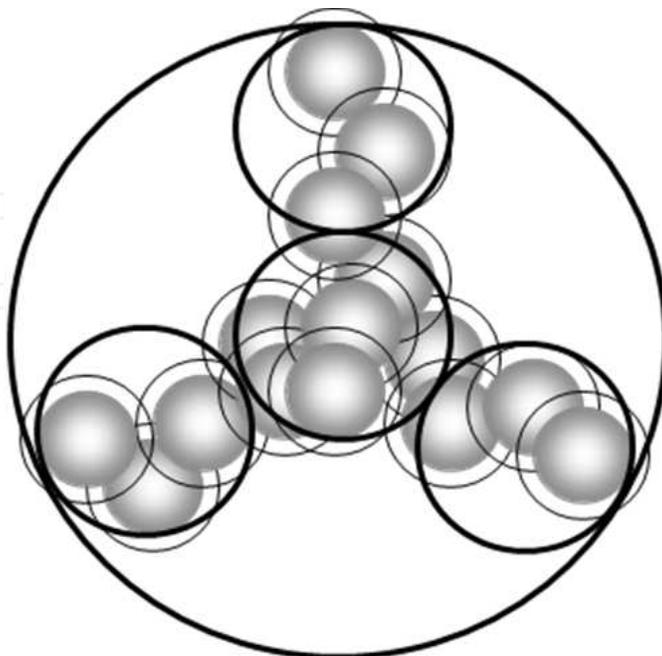


Fig. 1. Aggregate covering with spheres of changing radius.

The Hausdorff dimension (Hausdorff, 1919) is the critical exponent for which the Hausdorff measure  $M_d$ , being proportional to the product of number of spheres and a power of their radius, changes from zero to infinity when the size of covering elements tends to zero

$$M_d \propto N(\rho) \cdot \rho^d \xrightarrow{\rho \rightarrow 0} \begin{cases} 0, & d > D \\ \infty, & d < D \end{cases} \quad (1)$$

In practice each monomer has its size. It is thus generally accepted the constancy of Hausdorff measure in a finite range of size to be sufficient to characterize the aggregate structure. The constancy of the Hausdorff measure for two limiting sizes of spheres, written for an aggregate containing  $i$  monomers, can be expressed as

$$1 \cdot R^D = i \cdot R_1^D \quad (2)$$

where  $R$  is the radius of the sphere circumscribed on the aggregate and  $R_1$  is the radius of envelope surrounding one monomer, for which the similarity to the aggregate still exists (Gmachowski, 2002).

The structure of aggregates is permeable which means that a fluid flows not only around but also through the aggregate. It is analyzed by taking into account the internal permeability of aggregates, either directly or by replacing a given aggregate by a smaller impermeable sphere of the same hydrodynamic properties. In this way the hydrodynamic radius is defined.

The structure of fractal aggregate can be related to the possibility to penetrate its interior by a fluid, well represented by internal permeability. The translational friction coefficient of a particle of radius  $R$  can be written in the following form

$$f_T = 6\pi\eta_0 R \cdot \frac{r}{R} \quad (3)$$

where the hydrodynamic radius  $r$  is introduced to take into account its dependence on the internal permeability of the aggregate. Such relation gave Brinkman for translational friction factor (Brinkman, 1947)

$$\frac{r}{R} = \frac{1 - \frac{\tanh \sigma}{\sigma}}{1 + \frac{3}{2\sigma^2} \left(1 - \frac{\tanh \sigma}{\sigma}\right)} \quad (4)$$

where  $\sigma = R / \sqrt{k}$  is the reciprocal square root of dimensionless internal permeability of a sphere of uniform structure modeling the fractal aggregate. The analogous relations of the normalized hydrodynamic radius for the rotational friction coefficient and the intrinsic viscosity are slightly different, but all the three give the results which are very close to one another (Gmachowski, 2003).

For a homogeneous porous medium, being an arrangement of monosized particles, the permeability is proportional to the square of the characteristic pore size (Dullien, 1979) which is closely correlated to the size of constituents. In the case of fractal aggregate, which is not homogeneous, the fluid flow occurs mainly in the large pores. Hence their size determines the aggregate permeability.

For similar aggregates the size of large pores scales as the size of the whole aggregate. Therefore the ratio of the internal permeability and the square of aggregate radius is expected to be constant for aggregates of the same fractal dimension and to decrease with increasing fractal dimension due to the increment of the aggregate compactness (Gmachowski, 1999; Woodfield & Bickert, 2001; Bushell et al., 2002). This means that  $\sigma = R / \sqrt{k}$  is a unique function of the fractal dimension of an aggregate and hence the ratio  $r/R$  is determined by  $D$  (Eq. 4). A formula

$$\frac{r}{R} = \sqrt{1.56 - \left(1.728 - \frac{D}{2}\right)^2} - 0.228 \quad (5)$$

has been derived from analysis of permeability of aggregated system (Gmachowski, 2000) and is confirmed by different hydrodynamic properties of fractal aggregates (Gmachowski, 2003).

This means that the hydrodynamic radius is proportional to aggregate radius for a given fractal dimension. The covering can be thus performed not only in the range of radii, but also in the range of hydrodynamic radii. The hydrodynamic radius of a solid monomer is its geometrical radius. For fractal aggregate the mass-hydrodynamic radius relation has the following form

$$i = \left(\frac{r}{a}\right)^D \quad (6)$$

since the hydrodynamic radius  $r$  converges to the primary particle radius  $a$  for the number of constituent particles equal to unity (Gmachowski, 2008). The mass-radius relation reads

$$i = \left(\frac{r}{R}\right)^D \left(\frac{R}{a}\right)^D \quad (7)$$

which reduces to the previous one if the aggregation number is related to the hydrodynamic radius instead to the radius. The full form of mass-radius relation has the form

$$i = \left[ \sqrt{1.56 - \left(1.728 - \frac{D}{2}\right)^2} - 0.228 \right]^D \left(\frac{R}{a}\right)^D \quad (8)$$

Plotting in a log-log system the aggregation number against radius for several similar aggregates, one can determine a best fit straight line whose slope is the fractal dimension and the location makes it possible to determine the monomer radius.

If the aggregate is composed of smaller aggregates instead of solid monomers, their number is correlated to the hydrodynamic radius of smaller aggregates according to the mass-radius relation of the form similar to Eq. (8).

## 2. Aggregates with complex structure

An aggregate has a complex structure if it consists of smaller aggregates instead of solid monomers (Fig. 2) and their fractal dimension is different from that of the whole aggregate.

In opposite, the constancy of Hausdorff measure would take place in the range of the whole aggregate hydrodynamic size down to the solid monomer size. An aggregate with complex structure is termed as aggregate with mixed statistics, since it has different fractal dimensions on different length scales. The constituent aggregates are known as blobs.

The knowledge of the hydrodynamic radius in relation to the radius of fractal aggregate of a given fractal dimension, utilized for blobs, makes it possible to replace the blobs by their hydrodynamic equivalents. In this way an aggregate with mixed statistics is reduced to fractal aggregate with the Hausdorff measure constant in the range of the whole aggregate hydrodynamic size down to the hydrodynamic size of blobs.

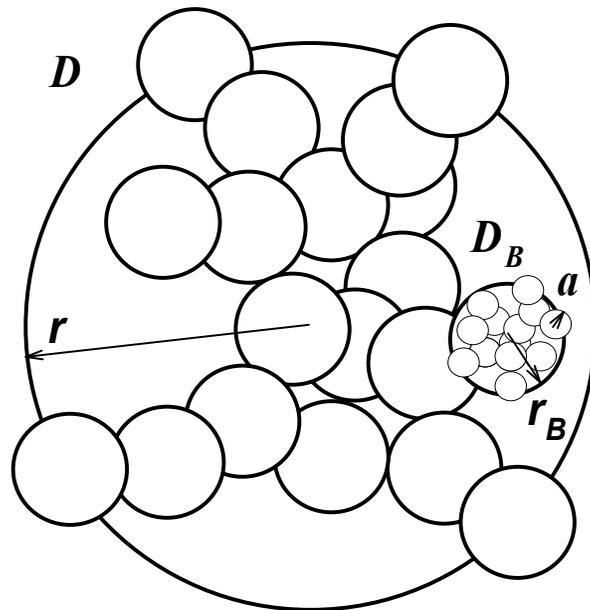


Fig. 2. Graphical representation of an aggregate with mixed statistics. The aggregate fractal dimension is a result of the spatial arrangement of blobs.

An aggregate with mixed statistics of hydrodynamic radius  $r$  and fractal dimension  $D$  consists of  $I$  blobs of hydrodynamic radius  $r_B$  and fractal dimension  $D_B$ , each containing  $i_B$  solid monomers of radius  $a$ . The mass-hydrodynamic radius relations are

$$i_B = \left( \frac{r_B}{a} \right)^{D_B} \quad (9)$$

$$I = \left( \frac{r}{r_B} \right)^D \quad (10)$$

Let us imagine an aggregate of the same mass and fractal dimension composed of monomers instead of blobs. Then the total number of monomers can be expressed as

$$I i_B = \left( \frac{r_0}{a} \right)^D \quad (11)$$

Combining the last three equations, one gets the expression for the change of hydrodynamic radius caused by the presence of blobs

$$\frac{r}{r_0} = i_B^{1/D_B - 1/D} \quad (12)$$

The corresponding mass-radius relation for an aggregate with mixed statistics reads

$$I = \left[ \sqrt{1.56 - \left(1.728 - \frac{D}{2}\right)^2} - 0.228 \right]^D \left(\frac{R}{r_B}\right)^D \quad (13)$$

which makes it possible to determine the blob hydrodynamic radius by plotting in a log-log system the number of blobs against the aggregate radius for several similar aggregates with mixed statistics and then deducing the slope and location of the best fit straight line obtained.

### 3. Asphaltene aggregates

The aggregate of mixed statistics can be obtained by shearing the crude oil (Gmachowski & Paczuski, 2011). Asphaltenes, a part of petroleum, are aromatic multicyclic molecules surrounded and linked by aliphatic chains and heteroatoms, of the molar mass in the range 500-50000 u. As a result of shearing, they aggregate to form blobs of a size of several micrometers, which join to form aggregates with mixed statistics. If the crude oil is mixed with toluene and n-heptane in different proportions, the range of aggregate size becomes wider.

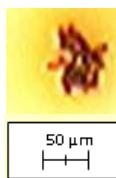


Fig. 3. Typical microscope image of asphaltene aggregate.

It is possible to estimate the size and number of blobs for several images (Fig. 3) to identify the form of mass-radius relation of asphaltene aggregates by plotting the data in a log-log system. This is presented in Fig. 4.

The fractal dimension determined by this method for aggregates of mixed statistics investigated was  $D=1.5$ , whereas the hydrodynamic radius of blobs  $r_B \cong 3\mu m$ . Two additional lines are drawn in Fig. 4, representing Eq. (13) for the same fractal dimension and two values of the blob hydrodynamic radius, namely  $r_B = 2\mu m$  and  $r_B = 4\mu m$ . Their locations do not correspond to points representing the experimental data, which confirms the rationality of the method of mass-radius relation for aggregates with mixed statistics. Moreover, the size estimated (blob hydrodynamic radius  $r_B = 3\mu m$ ) is close to that observed in the image (blob radius), which suggests very compact structure of blobs formed by asphaltenes.

### 4. Free settling velocity

Free settling velocity of an aggregate with mixed statistics can be determined by equating the gravitational force allowing for the buoyancy of the surrounding fluid with the opposing

hydrodynamic force which depends on the aggregate size and its permeability. The use of hydrodynamic radius which is the radius of an impermeable sphere of the same mass

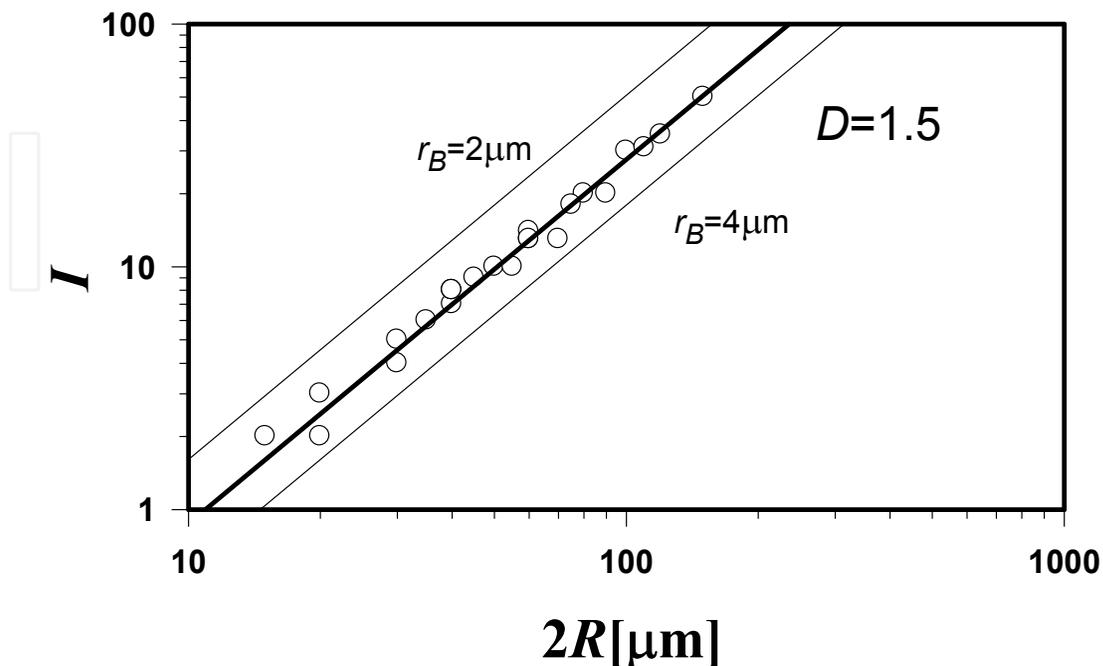


Fig. 4. Graphical representation of the mass-radius relation for asphaltene aggregates.

having the same dynamic properties, instead of the aggregate radius, makes it possible to neglect the internal permeability. For an aggregate of hydrodynamic radius  $r$  composed of  $i = Ii_B$  primary particles of radius  $a$  the force balance is

$$\frac{4}{3}\pi a^3 I i_B (\rho_s - \rho_f) g = 6\pi\eta_0 r u \quad (14)$$

Using the mass-hydrodynamic radius relations for blob and aggregate (Eqs. 9,10), one gets

$$\frac{u}{u_a} = I^{1-1/D} i_B^{1-1/D_B} \quad (15)$$

where

$$u_a = \frac{2}{9\eta_0} (\rho_s - \rho_f) g a^2 \quad (16)$$

is the Stokes falling velocity of primary particle.

Alternatively, using the expression for the hydrodynamic radius changed by the presence of blobs (Eq. 12), one obtains

$$\frac{u}{u_a} = \left(\frac{r_0}{a}\right)^{D-1} / \frac{r_0}{r} \quad (17)$$

If the blobs of the fractal dimension different from that of the aggregate are not present ( $D = D_B$  and  $r_0 = r$ ), the corresponding dependences reduce to the following relations

$$\frac{u_0}{u_a} = i^{1-1/D} \quad (18)$$

$$\frac{u_0}{u_a} = \left( \frac{r_0}{a} \right)^{D-1} \quad (19)$$

characteristic for fractal aggregates with one-level structure. Hence the following formulae

$$\frac{u}{u_0} = i_B^{1/D-1/D_B} \quad (20)$$

$$\frac{u}{u_0} = \frac{r_0}{r} \quad (21)$$

describe the free settling velocity of aggregates with mixed statistics.

### 5. Intrinsic viscosity of macromolecular coils and the thermal blob mass

A macromolecular coil in a solution is modeled as an aggregate with mixed statistics consisting of  $I$  thermal blobs of  $D_B = 2$ , each containing  $i_B$  solid monomers of radius  $a$  and mass  $M_a$ . To calculate the intrinsic viscosity

$$[\eta] \equiv \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 c} \quad (22)$$

one has to define the mass concentration  $c$  of a macromolecular solution analyzed. The mass concentration in the coil, represented by the equivalent impermeable sphere, can be calculated as the product of the total number of non-porous monomers  $I i_B$  multiplied by their mass  $4/3\pi a^3 \rho_s$  and divided by the hydrodynamic volume of the coil  $4/3\pi r^3$ . This concentration multiplied by the volume fraction of equivalent aggregates  $\varphi$  gives the overall polymer mass concentration in the solution.

$$c = \varphi \rho_s \frac{I i_B a^3}{r^3} \quad (23)$$

Mass-radius relations are then employed. The thermal blob mass related to that of nonporous monomer is the aggregation number of the thermal blob

$$i_B = \frac{M_B}{M_a} = \left( \frac{r_B}{a} \right)^2 \quad (24)$$

whereas the macromolecular mass related to that of thermal blob is the aggregation number of aggregate equivalent to coil

$$I = \frac{M}{M_B} = \left( \frac{r}{r_B} \right)^D \quad (25)$$

Taking into account that the volume fraction of polymer in an aggregate equivalent to polymer coil can be rearranged as follows

$$\frac{I_B a^3}{r^3} = I \left( \frac{r_B}{r} \right)^3 i_B \left( \frac{a}{r_B} \right)^3 \quad (26)$$

finally one gets

$$c = \varphi \rho_s \left( \frac{M_B}{M_a} \right)^{-1/2} \left( \frac{M}{M_B} \right)^{1-3/D} \quad (27)$$

or

$$c = \varphi \rho_s \left( \frac{M_B}{M_a} \right)^{-1/2} \left( \frac{M}{M_B} \right)^{-a_{MHS}} \quad (28)$$

if the fractal dimension  $D$  is replaced by the Mark-Houwink-Sakurada exponent  $a_{MHS}$ , characterizing the thermodynamic quality of the solvent, where

$$a_{MHS} = 3 / D - 1 \quad (29)$$

The structure of a dissolved macromolecule depends on the interaction with solvent and other macromolecules. The resultant interaction determines whether the monomers effectively attract or repel one another. Chains in a solvent at low temperatures are in collapsed conformation due to dominance of attractive interactions between monomers (poor solvent). At high temperatures, chains swell due to dominance of repulsive interactions (good solvent). At a special intermediate temperature (the theta temperature) chains are in ideal conformations because the attractive and repulsive interactions are equal. The exponent  $a_{MHS}$  changes from 1/2 for theta solvents to 4/5 for good solvents, which corresponds to the fractal dimension range of from 2 to 5/3.

The viscosity of a dispersion containing impermeable spheres present at volume fraction  $\varphi$  can be described by the Einstein equation (Einstein, 1956)

$$\eta = \eta_0 \left( 1 + \frac{5}{2} \varphi \right) \quad (30)$$

from which

$$\frac{\eta - \eta_0}{\eta_0} = \frac{5}{2} \varphi \quad (31)$$

The intrinsic viscosity can be thus calculated as

$$[\eta] \equiv \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 c} = \lim_{c \rightarrow 0} \frac{5}{2} \frac{\varphi}{c} \quad (32)$$

Utilizing the expression for the mass concentration, one gets

$$[\eta] \equiv \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 c} = \lim_{c \rightarrow 0} \frac{5}{2} \frac{\varphi}{c} = \lim_{c \rightarrow 0} \frac{5}{2} \frac{\varphi}{\varphi \rho_s \left(\frac{M_B}{M_a}\right)^{-1/2} \left(\frac{M}{M_B}\right)^{-a_{MHS}}} = \frac{5}{2\rho_s} \left(\frac{M_B}{M_a}\right)^{1/2} \left(\frac{M}{M_B}\right)^{a_{MHS}} \quad (33)$$

The obtained equation can be also derived in terms of complex structure aggregate parameters for any blob fractal dimension to get

$$[\eta] = \frac{5}{2\rho_s} i_B^{3/D_B - 1} l^{3/D - 1} \quad (34)$$

which is equivalent to

$$[\eta] = \frac{5}{2\rho_s} \left(\frac{r_0}{a}\right)^{3 - 1/D} \left(\frac{r}{r_0}\right)^3 \quad (35)$$

Equation derived for polymer coil can be compared to the empirical Mark-Houwink-Sakurada expression relating the intrinsic viscosity to the polymer molecular mass

$$[\eta] = K_\eta M^{a_{MHS}} \quad (36)$$

For the theta condition the formulae (Eq. 33) read

$$[\eta]_\theta = \frac{5}{2\rho_s} \left(\frac{M_B}{M_a}\right)^{1/2} \left(\frac{M}{M_B}\right)^{1/2} = \frac{5}{2\rho_s} \left(\frac{M}{M_a}\right)^{1/2} \quad (37)$$

and

$$[\eta]_\theta = K_\theta M^{1/2} \quad (38)$$

The Mark-Houwink-Sakurada expressions are presented in Fig. 5.

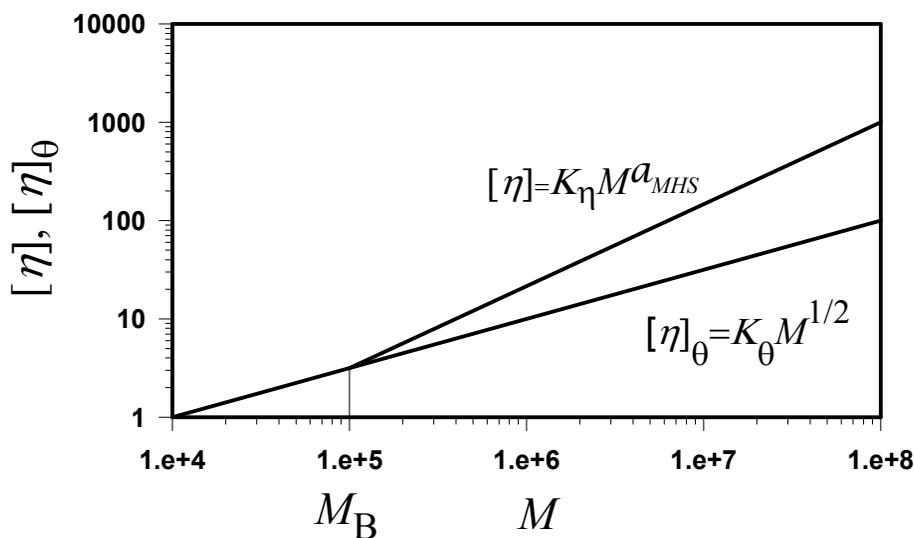


Fig. 5. Graphical representation of the Mark-Houwink-Sakurada expressions.

There is a lower limit of the Mark-Houwink-Sakurada expression applicability. Intrinsic viscosity of a given polymer in a solvent crosses over to the theta result at a molecular mass which is the thermal blob molecular mass. This means that

$$K_{\eta}M_B^{a_{MHS}} = K_{\theta}M_B^{1/2} \quad (39)$$

from which

$$M_B = \left( \frac{K_{\theta}}{K_{\eta}} \right)^{1/(a_{MHS}-1/2)} \quad (40)$$

The thermal blob mass depends on the Mark-Houwink-Sakurada constant at the theta temperature, characteristic for a given polymer-solvent system, as well as the constant and the Mark-Houwink-Sakurada exponent valid at a given temperature. The form of this dependence is strongly influenced by the mass of non-porous monomer  $M_a$  of thermal blobs, which is different for different polymers. The thermal blob mass normalized by the mass of non-porous monomer  $M_B / M_a$ , however, is the number of non-porous monomers in one thermal blob and therefore it is expected to be a unique function of the solvent quality. This function, determined (Gmachowski, 2009a) from many experimental data measured for different polymer-solvent systems, reads

$$i_B = \frac{M_B}{M_a} = \left\{ \exp \left[ 0.9 \cdot (2a_{MHS} - 1)^{1/3} \right] \right\}^{a_{MHS}/(a_{MHS}-0.5)} \quad (41)$$

The thermal blob aggregation number can be also calculated from the theoretical model of internal aggregation based on the cluster-cluster aggregation act equation (Gmachowski, 2009b)

$$i + i \sim \left[ \frac{r}{R}(D) \right]^D \left( i^{1/D_i} + i^{1/D_i} \right)^D \quad (42)$$

being an extension of the mass-radius relation for single aggregate

$$i = \left( \frac{r}{a} \right)^D = \left[ \frac{r}{R}(D) \right]^D \left( \frac{R}{a} \right)^D \quad (43)$$

assuming it is a result of joining to two identical sub-clusters and its radius  $R$  is proportional to the sum of hydrodynamic radii  $a \cdot (i^{1/D_i} + i^{1/D_i})$ , where the normalized hydrodynamic radius is described by Eq. (5). Aggregation act equation can be specified to the form of an equality

$$i_B + i_B = 2^{1-D} \left[ \frac{r}{R}(D) / \frac{r}{R}(D_{\text{lim}}) \right]^D \left( i_B^{1/D_i} + i_B^{1/D_i} \right)^D \quad (44)$$

for which  $D$  tends to  $D_{\text{lim}}$  if  $i_B$  tends to infinity.

Let us imagine a coil consisting of one thermal blob. This is in fact a thermal blob of the structure of a large coil. Such rearranged blobs can join to another one to produce an object of double mass. The model makes it possible to calculate the fractal dimension  $D$  of the coil after each act of aggregation of two smaller identical coils of fractal dimension  $D_i$  changing with the aggregation progress.

Using the model for  $D_{lim} = 2$  (the fractal dimension of thermal blobs), the dependences  $i_B(D)$  have been calculated using CCA simulation, starting from both good and poor solvent regions. The aggregates growing by consecutive CCA events restructured to get a limiting fractal dimension  $D_{lim}$  in an advanced stage of the process. Starting from  $i_B = 8$  and  $D_i = 5/3$ , the result is  $D = 1.8115$ . The second input to the model equation is thus  $i_B = 16$  and  $D_i = 1.8115$ . Finally, the calculation results are presented in Fig. 6, where they are compared to the dependence deduced from the empirical data.

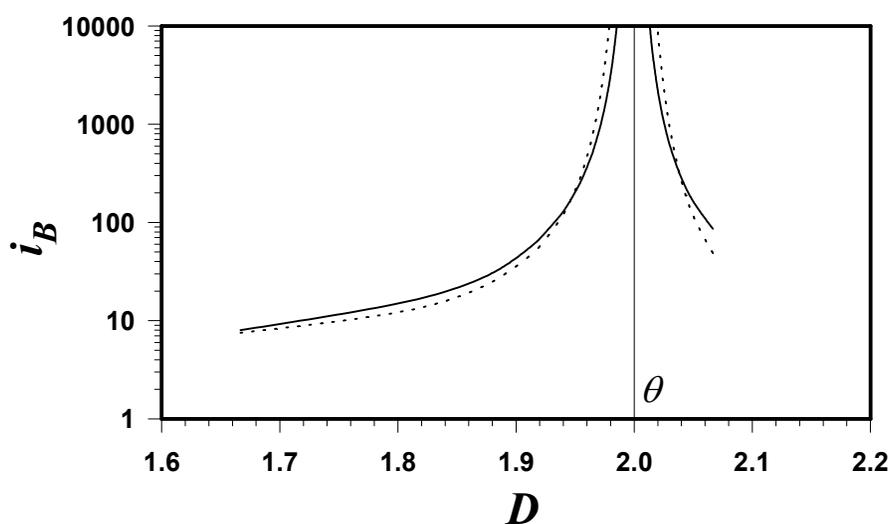


Fig. 6. Comparison of the model fractal dimension dependence of the thermal blob aggregation number (solid lines) to the representation of the experimental data measured for different polymer-solvent systems (Eq. 41), depicted as dashed lines.

## 6. Hydrodynamic structure of fractal aggregates

As discussed earlier, the ratio of the internal permeability and the square of aggregate radius is expected to be constant for aggregates of the same fractal dimension. Consider an early stage of aggregate growth in which the constancy of the normalized permeability is attained. At the beginning the aggregate consists of two and then several monomers. The number of pores and their size are of the order of aggregation number and monomer size, respectively. At a certain aggregation number, however, the size of new pores formed starts to be much larger than that formerly created. This means that the hydrodynamic structure building has been finished and the smaller pores become not active in the flow and can be regarded as connected to the interior of hydrodynamic blobs.

A part of the aggregate interior is effectively excluded from the fluid flow, so one can consider this part as the place of existence of impermeable objects greater than the monomers. Since both the impermeable object size and the pore size are greater than formerly, the real permeability is bigger than that calculated by a formula valid for a

uniform packing of monomers. So this point can be considered as manifested by the beginning of the decrease of the normalized aggregate permeability calculated.

During the aggregate growth the number of large pores tends to a value which remains unchanged during the further aggregation. The self-similar structure exists, which can be described by an arrangement of pores and effective impermeable monomers (hydrodynamic blobs) of the size growing proportional to the pore size.

According to the above considerations one can expect effective aggregate structure such that the normalized aggregate permeability  $k/R^2$  attains maximum. To determine the hydrodynamic structure of fractal aggregate the aggregate permeability is estimated by the Happel formula

$$\frac{k}{a^2} = \frac{2}{9\varphi} \cdot \frac{3 - 4.5\varphi^{1/3} + 4.5\varphi^{5/3} - 3\varphi^2}{3 + 2\varphi^{5/3}} \quad (45)$$

where the volume fraction of solid particles in an aggregate is described as

$$\varphi = i \cdot \left(\frac{a}{R}\right)^3 \quad (46)$$

The normalized aggregate permeability is calculated as

$$\frac{k}{R^2} = \frac{k}{a^2} \frac{a^2}{R^2} = \frac{k}{a^2} \left(\frac{i}{\varphi}\right)^{-2/3} \quad (47)$$

The results are presented in Fig. 7.

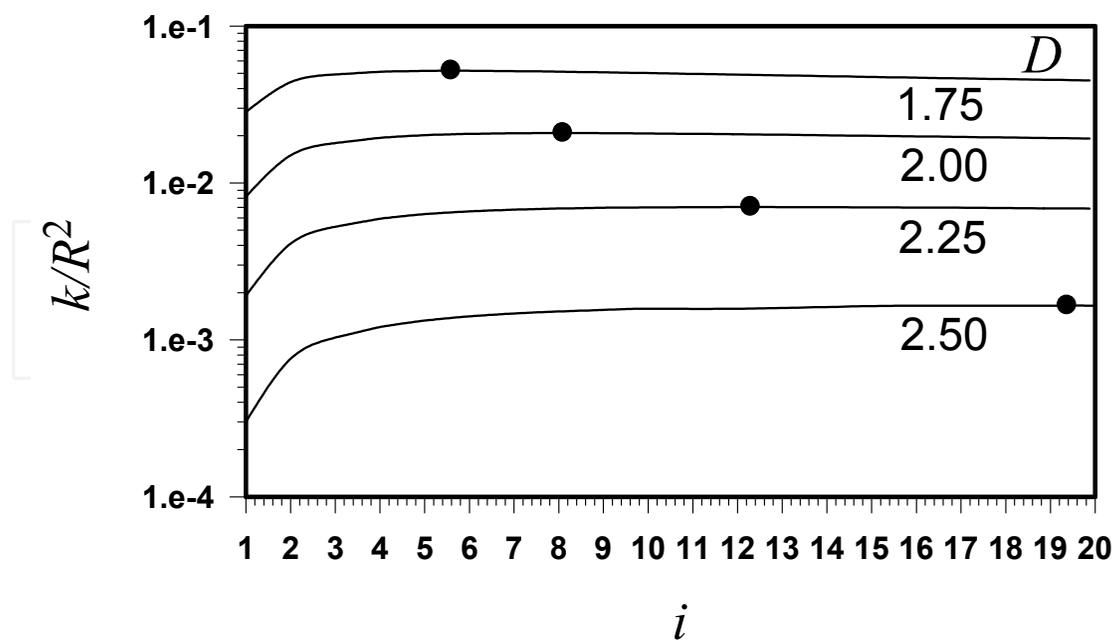


Fig. 7. Normalized aggregate permeability calculated by the Happel formula for different fractal dimensions. The maxima (indicated) determine the number of hydrodynamic blobs in aggregate.

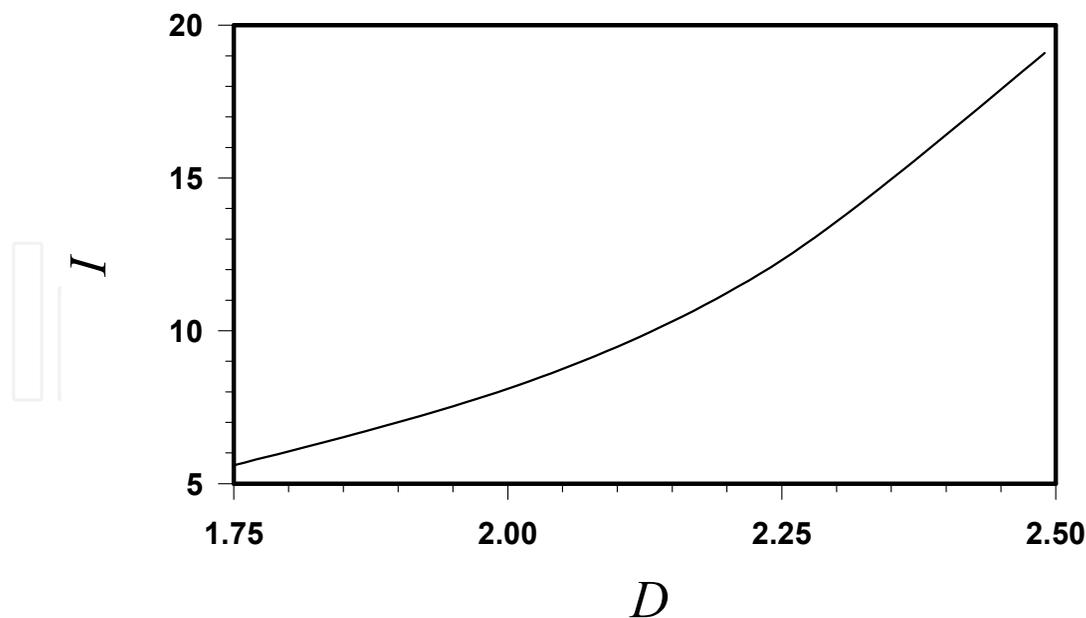


Fig. 8. Number of hydrodynamic blobs as dependent on fractal dimension.

Due to self-similarity, the number of monomers deduced from Fig. 8 is the number of hydrodynamic blobs which are the fractal aggregates similar to the whole aggregate. Hydrodynamic picture of a growing aggregate is such that after receiving a given number of monomers the number of hydrodynamic blobs becomes constant and further growth causes the increase in blob mass not their number.

As this estimation shows, the number of hydrodynamic blobs rises with the aggregate fractal dimension. The knowledge of this number makes it possible to estimate the aggregate permeability in the slip regime where the free molecular way of the molecules of the dispersing medium becomes longer than the aggregate size. In this region the dynamics of the continuum media is no longer valid.

The permeability of a homogeneous arrangement of solid particles of radius  $a$ , present at volume fraction  $\varphi$ , can be calculated (Brinkman, 1947) as

$$\frac{k}{a^2} = \frac{2}{9\varphi} \cdot \frac{6\pi\eta_0 a}{f_{packing}} \quad (48)$$

The friction factor of a particle in a packing can be presented as the friction factor of individual particle multiplied by a function of volume fraction of particles

$$f_{packing} = f \cdot S(\varphi) \quad (49)$$

In the continuum regime

$$f = f_{continuum} = 6\pi\eta_0 a \quad (50)$$

whereas in the slip one (Sorensen & Wang, 2000)

$$f = f_{slip} = 6\pi\eta_0 a / \left( 1 + 1.612 \frac{\lambda}{a} \right) \quad (51)$$

where  $\lambda$  is the gas mean free path.

For a given structure of arrangement  $(a, \varphi)$  it possible to calculate the permeability coefficient in the slip regime from that valid in the continuum regime (Gmachowski, 2010)

$$k_{slip} = k \frac{f_{continuum}}{f_{slip}} = \left( 1 + 1.612 \frac{\lambda}{a} \right) \cdot k \quad (52)$$

in which the monomer size should be replaced by the hydrodynamic blob radius rising such as the growing aggregate. So large differences in permeabilities at the beginning diminish when the aggregate mass increases and disappear when the aggregate size greatly exceeds the gas mean free path.

Calculated mobility radius  $r_m$ , representing impermeable aggregate in the slip regime, is smaller than the hydrodynamic one because of higher permeability and tends to the hydrodynamic size when the difference in permeabilities becomes negligible. At an early stage of the growth of aerosol aggregates it can be approximated as a power of mass (Cai & Sorensen, 1994)

$$r_m = a \cdot i^{1/2.3} \quad (53)$$

in which the number 2.3 greatly differs from the fractal dimension equal to 1.8.

## 7. Discussion

Covering the aggregate with spheres of a given size, one defines the blobs which are the units in which the monomers present in aggregates are grouped. Changing the size of the spheres we can increase or decrease the blob size. If the blobs have the same structure as the whole aggregate, the aggregate is the self-similar object.

Otherwise the object is a structure of mixed statistics with the hydrodynamic properties described in this chapter. There were analyzed aggregates containing monosized blobs of a given fractal dimension. The blobs of asphaltene aggregates are dense, probably of fractal dimension close to three. The thermal blobs - the constituents of polymer coils - have constant fractal dimension of two, independently of the thermodynamic quality of the solvent and hence the coil fractal dimension.

The determination of the hydrodynamic radius of hydrodynamic blobs in fractal aggregates, despite the same fractal structure as for the whole aggregate, serves to estimate the size of large pores through the fluid can flow. It makes it possible to model the fluid flow through the aggregate in terms of both the continuum and slip regimes.

## 8. References

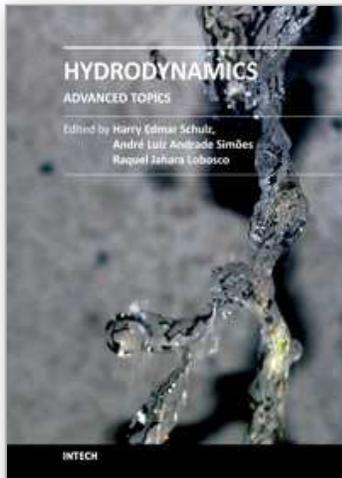
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Edited by Prof. Harry Schulz

ISBN 978-953-307-596-9

Hard cover, 442 pages

**Publisher** InTech

**Published online** 22, December, 2011

**Published in print edition** December, 2011

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