The role of surface roughness on the effective interactions and phase behaviour of calcium carbonate nanoparticles

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Abstract

The stability of nanoparticle suspensions is determined by a subtle interplay of particle-particle and particle-solvent interactions. Experimental studies of suspensions of calcite nanoparticles have reported formation of gels, hence providing evidence for adhesive interactions. Data obtained using extended calcite surfaces support the existence of repulsion between surfaces, which has been assigned to the presence of surface roughness. Here, we use the Derjaguin approximation to calculate the effective interactions between calcite nanoparticles as a function of their inter-particle separation and incorporating surface roughness effects. We combine an approach based on a Gaussian distribution of surface heights with surface-surface interactions obtained recently in flat surfaces using molecular simulations [G. Svaland and F. Bresme, J. Phys. Chem. C, 2018, 122 (13), pp 7321-7330]. We show that roughness effects associated to a discrete distribution of heights, such as atomic steps or terraces in mineral surfaces, results in very different effective inter-colloidal potentials. Using Langevin computer simulations and the effective inter-particle potentials we demonstrate that roughness
effects might influence significantly the phase behaviour of nanoparticle suspensions. Small roughnesses lead to the formation of gel structures, while stable dispersed suspensions are obtained when the root-mean-squared deviation (RMSD) of the surface roughness increases above a \( \sim 0.25 \) Å threshold.

Nanoparticle suspensions are widely used in soft materials; food stuffs, pharmaceuticals, or high performance fluids, such as nanofluids. Suspensions of mineral nanoparticles, such as calcium carbonate, are important in the manufacture of cements used in the construction industry. Calcite powders, consisting of particles with diameters varying from 100’s of nm to µm, can be dispersed in water to make pastes, which are used in the manufacture of paper as well as in building materials. The interactions between the colloids determines the phase stability, structure and rheological properties of the suspension. Hence an understanding of the microscopic mechanisms defining the inter-colloidal interactions between mineral nanoparticles is of key importance.

Calcite surfaces are prone to dissolution and crystallization. These processes play an important role in the reconstruction of the surface and defines its roughness. Roughness effect can potentially modify the effective interaction between the surfaces. This notion has been tested recently in experiments of extended calcium carbonate surfaces, using the surface forces apparatus. The experiments indicate that the inter-surface interactions are repulsive when the surfaces are immersed in water. Experiments of aqueous suspensions containing calcium carbonate nanoparticles with diameters of 60 nm, demonstrated the formation of gel phases. Gel phases are associated to adhesive inter-particle interactions, hence these experiments do also support the existence of attractive interactions between calcium carbonate surfaces, at least in suspensions of small nanoparticles. The strengthening of calcium carbonate pastes obtained from recrystallization of amorphous calcium carbonate and vaterite mixtures has been associated to the smoothing of surfaces at grain contacts. Recent molecular dynamics simulations of flat calcium carbonate surfaces immersed in water do also provide support for attractive interactions. Strong adhesive minima were observed at inter-
surface separations of about 1 nm. The adhesion is driven by both direct surface-surface interactions and also by the solvation layer of water attached to the surfaces. Shifts in the relative position of the surface planes have a large impact on the interaction strength, highlighting the important role of the surface properties in defining solvent mediated interactions between mineral surfaces. While the simulation results and the behaviour of nanoparticle suspensions are consistent with each other in terms of the dominant role of attractive interactions between surfaces, the experiments on extended surfaces revealed the importance of repulsive interactions. We believe that the consideration of surface roughness can help to explain these contrasting results.

The theoretical description of surface roughness requires an extension of the existing theoretical models, such as the DLVO theory. Roughness effects have been used to explain colloidal stability, which was not predicted by the standard DLVO theory. Surface and chemical heterogeneities were identified as potential contributors to the discrepancies between theory and experiments, prompting the implementation of surface roughness in theoretical models. These works showed that the incorporation of roughness leads to strong changes in the inter-colloidal interactions, relative to the DLVO predictions.

Here, to assess the impact of roughness on the interactions between calcite nanoparticles, we adopt a convolution approach that builds on the model developed by Parsons et al., whereby the force between flat surfaces is convoluted with a probability distribution that defines the roughness of the surface of interest. A key input for this approach is the solvent mediated interactions between flat calcite surfaces, which were computed recently using state of the art forcefields and molecular simulations. We use the resulting effective potentials to investigate with Langevin dynamics computer simulations the phase behaviour of colloidal suspensions. We find that the surface roughness has a profound impact on the nature of adhesive minimum found in flat surfaces. The minimum disappears in rough colloids, even for small RMSD roughnesses of the surface ~ 0.25 nm, and the effective interaction becomes repulsive. We predict that suspensions consisting of calcite nanoparticles with rough surfaces
are stable, while smooth surfaces, such as those present in faceted nanoparticle should lead to nanoparticle aggregation into fractal structures, and ultimately formation of gel phases. The formation of gel like structures is consistent with recent experiments of suspensions containing calcium carbonate nanoparticles.

**Free energies of flat surfaces** We employed for our analysis the free energy of interaction between flat calcium carbonate surfaces reported recently in reference. The free energy curve was computed by sampling the interaction forces at different inter-surface forces, and then integrating the forces between specific separations, $r_0$ and $r$, $\Delta F(r) = F(r) - F(r_0) = -\int_{r_0}^{r} f(s)ds$, where $f(s)$ is the total force acting on the surfaces as a function of the inter-surface separation, $r$. $r_0$ is a reference distance defining the zero of the free energy at long distances.

We have reproduced in Fig. 1 the interaction free energy of two flat calcite surfaces corresponding to the (10\bar{1}4) plane. The main feature of the free energy is the existence of a
strong adhesive minimum at $r < 1$ nm, which arises from the overlap of the water solvation layers attached to the calcite surfaces. The double layer repulsion arising from the calcite surface charge is expected to be much smaller than the solvation forces at nanometer inter-surface separations, given the low surface potential of calcite (-0.02 C/m$^2$), and therefore should contribute little at this range of distances.

**Theoretical model to include roughness effects** We incorporate the roughness effects over mesoscopic length scales by using the Derjaguin approximation. The force, $F_h$, between two spherical particles is defined in terms of the inter-surface distance $h$. This force is determined by the interaction energy per unit area between two flat surfaces $W(h)$:

$$F(r) = 2\pi R_{eff}W(r)$$

where $R_{eff}^{-1} = R_1^{-1} + R_2^{-1}$ is the effective radius of curvature, with $R_1$ and $R_2$ the radii of the interacting spherical particles. The interaction energy between the two colloids can then be obtained from:

$$U(r) = -\int_{r_0}^{d} F(r)dr + U(r_0)$$

where $U(h_0)$ is an integration constant that defines the zero of energy for the potential at large inter-colloidal distances.

To understand the role of the roughness on the inter-particle interactions we introduce a height function, $f_h$, which follows the Gaussian distribution:

$$f_h = \frac{e^{-h^2/(2\rho^2)}}{\rho\sqrt{2\pi}}$$

where $r$ represents the surface-to-surface distance, $h$ represents the deviation from the reference surface $r$, and $\rho$ is the standard deviation that quantifies the degree of roughness of the surface. $\rho = 0$ corresponds to a flat surface. Combining Eqn. (3) with the Derjaguin
equations (1) and (2), we obtain a “roughened” Derjaguin approximation:

\[
F_r(r) = 2\pi R_{\text{eff}} \int_{-\infty}^{\infty} W(r) \frac{e^{-(h-r)^2/(2\rho^2)}}{\rho \sqrt{2\pi}} \, dr \tag{4}
\]

This approach has been pioneered by Parsons et al. to incorporate surface roughness in the theoretical calculation of surface forces. These authors showed that roughness amplifies the long range behaviour of DLVO forces, and shifts the repulsive branch detected in surface force measurements to a longer distance. The shift scales with the Root Mean Square roughness of the surfaces.

The crystalline surface of CaCO\textsubscript{3} features steps, as revealed by AFM experiments (see Figs. 2A and 2B). To model this surface topography we implemented a discrete Gaussian distribution of surface heights by using a step size of 0.3 nm, which corresponds to the height of a monolayer of CaCO\textsubscript{3} on the (10\overline{1}4) calcite surface. We calculated the interaction potentials as a function of the surface roughness for both distributions, the continuous distribution described by equation (3) and the discrete one (see Supplementary information).

**Impact of roughness on nanoparticle-nanoparticle interactions** Starting from the surface free energy profiles for two atomically flat calcium carbonate surfaces shown in Fig. 1, we calculated, using the Derjaguin approximation and Eq. (2) the interaction potential as a function of the centre-to-centre distance between nanoparticles of size \(\sigma = 60\) nm, hence following the experimental system studied in reference. We show in Fig. 2D the interaction potentials for different values of surface roughness. The results are represented in reduced units namely, \(U^* = U/kT\) with \(T = 300K\), and \(r^* = r/\sigma\), where \(\sigma\) is the nanoparticle diameter.

For particles without surface roughness, \(\rho = 0\), we observe a strong and narrow potential well. The well depth increases linearly with the size of the particle following Eq. (1). For the experimentally available \(\sigma = 60\) nm particle, the situation is reminiscent of the adhesive hard-sphere model, with a short-ranged attractive well on the order of 10’s \(k_B T\), or
Figure 2: AFM images of a calcite (10\bar{1}4) surface in A) deionized water and B) supersaturated solution with respect to calcite. The arrows indicate the crystallographic directions of terrace growth. Reprinted with permission from Vavouraki et al., Crystal Growth and Design 2010, 10, 160-69. Copyright 2010 American Chemical Society. C) Schematic representation of our model for a rough nanoparticle. The different surface heights result in an average inter-particle interaction given by the “roughened” Derjaguin approximation in Eq. 1, which averages the interaction of different surface heights (see detail of surface in zoomed image) by their probability distribution. D) Inter-particle interactions for continuous and discrete surface height distributions, as a function of the particle roughness (increasing $\rho$ from bottom to top). E) A randomly generated 2D surface with characteristic RMS surface roughness of $\rho$ =0.3 nm. The dotted lines represent the discrete surface heights using a step 0.3 nm, corresponding to the height of a monolayer of CaCO$_3$ on the (1014) calcite surface.

patchy colloidal potentials which feature similar interaction strengths.\cite{24,25} Hence, we expect that the effective interaction obtained here should lead to irreversible and diffusion-limited cluster aggregation (DLCA),\cite{23} forming a gel phase at low particle packing fractions, likely in the interval $\phi = 0.01 – 0.10$.\cite{24}

The strength of the primary attractive minimum decreases significantly with increasing roughness, irrespective on whether the roughness is modelled using the continuous or the discrete model. Our model shows that the type of roughness does also influence the shape of the interaction curve. A discrete distribution, mimicking the behaviour in calcite surfaces,
might lead to a shift of the repulsive branch to longer distances leading to a secondary
minimum, which upon increasing the roughness further becomes a primary minimum. This
minimum is however weaker, \(\sim 30k_BT\) than the primary minimum for the surface with no
roughness, \(\sim 130k_BT\). Based on our calculations, roughnesses of the order of \(\rho \sim 0.3\) nm
would result in a purely repulsive interaction.

**Impact of roughness on the phase behaviour of colloidal suspensions**
Following the analysis of the effective nanoparticle interaction with roughness, we investigated the
phase behaviour of the suspension by performing Langevin dynamics computer simulations
(details on the simulation set up are provided in the *Simulation methods* section, as well as
in the Supplementary Information). Starting from initial configurations with a random dis-
tribution of colloids, we performed simulations over trajectories spanning times of \(t^* = 10^3\),
which correspond approximately to 650 \(\tau_D\), where \(\tau_D = R^2 / D\) and \(R\) and \(D\) are the particle
radius and the diffusion coefficient. The time for an experimental system can be estimated
considering the diffusion coefficient of the colloids, \(D\), \(\tau_D = R^2 / D = R^3 \pi \eta / k_BT \sim 0.1\) ms,
using the viscosity of water at 300 K and the diameter of the colloids used in the experi-
ments, \(60\) nm.

Depending on the surface roughness, the colloids remained in a stable suspension (Fig.
3A) or aggregated into fractal clusters (see Fig. 3B and C). We also found that the interplay
of the roughness and the adhesive force led to the formation of compact spherical aggregates
(see Fig. 3D).

To quantify the nanostructure of the nanoparticle suspensions we computed the mean
cluster size, employing a distance criterion to construct the clusters. Two nanoparticles \(i\)
and \(j\) were assigned to the same cluster if their distance \(d_{ij} < 1.01\sigma\). At this distance
the interaction potential for the smooth and rough cases is on the order of \(\sim k_BT\) (see
Figure 2-D). The mean cluster size distribution, \(\langle s \rangle\), was computed using the equation.
Figure 3: Characteristic structures of the suspension depending on volume fraction and surface roughness. A) Particles at packing fraction $\phi = 0.05$, with continuous surface roughness of $\rho = 0.3$ nm, showing a non-aggregating suspension. B) Particles at packing fraction $\phi = 0.03$, with continuous surface roughness of $\rho = 0.15$ nm, showing the formation of individual clusters. C) Particles at packing fraction $\phi = 0.05$ and no surface roughness, showing a percolating gel. In panels B-D particles the colors indicate particles that belong to the same cluster. D) For a surface roughness of $\rho = 0.23$, the adhesive energy is low enough such that the clusters reorganize into a more compact structure (here $\phi = 0.10$). E) Logarithm of the mean cluster size normalized by the number of particles, $\ln\left(\langle s \rangle / N\right)$, as a function of particle roughness $\rho$ and volume fraction $\phi$, for a continuous surface height distribution. The lines indicate the approximate location of the boundary regions.

$$
\langle s \rangle = \frac{\sum_{s=1}^{s_{\text{max}}} s^2 P(s)}{\sum_{s=1}^{s_{\text{max}}} s P(s)}
$$

where $s$ is the cluster size, $P(s)$ is the cluster size probability distribution and the sums run over all clusters from size 1 up to the maximum size, $s_{\text{max}}$, observed in the simulations.

**Fractal dimension vs. surface roughness** To characterize the structure of the suspensions we computed the fractal dimension. The fractal dimension can be obtained from
the analysis of light scattering experiments, hence providing a reference to compare experiments and simulations. The Hausdorff fractal dimension was computed using the box counting algorithm.

In this method, the simulation box is divided into an integer number of cells, \( n \), giving a box length \( l = L/n \). The number of occupied cells \( N_f \) is then counted as a function of the box length \( l \) (see SI for an example of this calculation). The fractal dimension, \( d_f \), is then calculated from:

\[
d_f = \frac{\ln N_f(l)}{\ln(1/l)}
\] (6)

The fractal dimension of the suspension was averaged for clusters with number of particles \( s > 20 \), with a similar expression to Eq. (5):

\[
\langle d_f \rangle = \frac{\sum_{s=1}^{s_{\text{max}}} d_f s P(s)}{\sum_{s=1}^{s_{\text{max}}} s P(s)}
\] (7)

Following the work of Griffiths et al., we characterize the fractal dimension at two scales. The first scale corresponds to box sizes with a similar size to the characteristic size of the particle \( l = [1\sigma, 5\sigma] \), and it probes the local structure of the colloidal cluster. This length scale characterizes the degree of compactness of individual clusters. A second scale corresponds to box counting cell sizes in the range \( l = [5\sigma, L] \), where \( L \) is the size of the simulation box. This length scale quantifies the amount of volume in the simulation box that is occupied by each cluster, and therefore it is related with the percolation of the clusters.

We show in Fig. 4 the global and local fractal dimensions for the continuous surface roughness, as a function of \( \rho \) and \( \phi \). The global fractal dimension reveals that at increasing volume fractions the clusters fill the space more efficiently (large fractal dimension), generating percolating structures. This observation agrees with Fig. 3E, which predicts a percolation threshold between \( \phi = 0.04 - 0.05 \).

The analysis of the local fractal dimension shows that increasing the volume fraction
Figure 4: Global (Left panels) and local (right panels) fractal dimensions for continuous (A, B) and discrete (C,D) surface height distributions. The discrete surface roughness shows a shift in the percolation threshold, as well as a higher degree of cluster compaction between the percolating gel and fluid phases, connected to aggregation in the secondary minimum (indicated by the red arrows). The color maps were constructed using a running average over 5 points.

... does also increase the degree of compactness of the clusters, varying between $d_F \sim 1.5$ and $\sim 1.7$. This variation can be also seen in the emerging structures shown in Fig. 3, where the individual clusters below the percolation threshold are more elongated in nature.

We show in Figure 4 a colour map that illustrates the range of fractal dimensions in the roughness/packing fraction plane. For volume fractions $\phi > 0.05$ and roughness values $\sim 0.25$ nm, the structures transition from a percolating gel to a fluid phase. This region of the phase diagram is characterized by an increase in the local fractal dimension, $d_f \sim 1.8$ (see arrows in Figure 4). The increase in the fractal dimension reflects an increase in the degree of compaction of the clusters, which arises as a consequence of the weaker attractive interaction. The reduction in the interactions allows the clusters to rearrange themselves...
into more compact structures, specifically crystalline structures, as shown in Fig. 3-D. Aggregation into local crystalline structures as opposed to the formation of a percolating gels, has also been observed by Griffiths and coworkers using the Morse pair potential with different interaction strengths. Those authors reported local fractal dimensions similar to the ones we find in here.

The type of surface, either step or continuous, does also influence the shape of the clusters, as evidenced by the different fractal dimension diagrams (c.f. Figure 4 A, B and C, D). For discretized surfaces corresponding to a surface height distribution that takes stepwise values only, the transition between the percolating gel and the fluid phase is shifted to larger values of surface roughness, while the degree of compaction is larger. The key difference between the continuous and discrete surface height distributions can be understood by examining the inter-particle potentials reported in Fig. 2D. The interaction corresponding to the discrete distribution features a secondary minimum that leads to flocculation and less sparse clusters (see Fig. 2D). Our results therefore indicate that both the magnitude and the nature of the surface roughness can influence the phase behaviour and the structural properties of nanoparticle suspensions.

**Conclusions** In summary, we have investigated the stability of colloidal nanoparticles made of calcium carbonate using effective potentials that allow a systematic investigation of the influence of surface roughness in the phase behaviour of the suspension. We found that roughness has a large impact on the inter-colloidal interactions and therefore on the stability of the suspensions. Small roughness leads to strong aggregation and gel formation as observed in experiments of calcite nanoparticles. The fractal dimension of the clusters obtained in this way is comparable to the diffusion-limited cluster aggregation fractal dimension of $\sim 1.75$. Increasing the roughness leads to a shift of the effective repulsion to longer distances and to the stabilization of the suspension, enabled by the dominant role of repulsive interactions. Alternatively the formation of strong secondary minima stabilizes globular clusters with
crystalline structure. The repulsive interaction induced by roughness is consistent with the behaviour observed in extended surfaces, using e.g., the Surface Force Apparatus. Our work shows both attraction or repulsion between calcite surfaces can be recovered with the same underlying interactions when the roughness of the surface is taken into account. We expect this work will serve to rationalize existing contrasting observations, as well as to connect the phase behaviour of suspensions to the surface topography and volume fraction of the suspension. Our phase diagram (Figure 3-E) provides a route to establish this connection.

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Simulation methods We study a system of $N = 10000$ nanoparticles in a solvent represented as a continuum, using Langevin dynamics. The particles are randomly inserted in a simulation box of volume, $V$, according to the packing fraction of the suspension given by $\phi = (\pi\sigma^3 N)/(6V)$. The inter-particle interactions were defined using different types of roughness, namely, a continuous or discrete Gaussian distribution of surface heights, as discussed in the main text. The damping parameter $\tau = m/\zeta$ for the thermostat is estimated based on the viscosity of the fluid. For water, $\eta = 8.90 \times 10^{-4}$ Pa s. Using the definition of the friction coefficient, $\zeta = 3\pi\eta\sigma$, gives $\tau_{\text{water}}^* \approx 8 \times 10^{-4}$ in reduced units which corresponds to 0.6 ns, considering the density of calcite $2710$ kg/m$^3$, and a nanoparticles of diameter 60 nm.

We used the thermostat for the Langevin equations of motion proposed by Bussi and Parrinello, as implemented in LAMMPS. Due to the very steep and short range interactions, a very small timestep must be used to ensure accurate integration. To select the simulation time step, we use the conservation of effective energy, defined as $\tilde{H} = E_{\text{tot}} - \Delta E_{\text{stat}}$, where
$E_{tot}$ is the total energy of the system and $\Delta E_{tstat}$ is the increment in the energy due to the thermostat. $\tilde{H}$ was monitored for different values of timestep and damping parameters, for the smooth potential of particles with $\sigma = 60$nm. We find effective energy conservation for $\Delta t = 5 \times 10^{-6}$ (see Fig. 1 in the Supplementary Information), in a range of damping parameters 1-100 $\tau_{water}$, see Supplementary Information. Larger damping parameters correspond to lower viscosities, thus effectively increasing the efficiency of the simulation. For this reason, we set $\tau = 100 \tau_{water}$. We note that the change in the effective viscosity does not influence the final structure of the colloidal suspension.
Supplementary information

Probability distribution of surface heights

The continuous probability distribution for the surface heights follows a Gaussian distribution, given by:

\[ f_h = \frac{e^{-(h-r)^2/(2\rho^2)}}{\rho\sqrt{2\pi}} \]  

where \( r \) is the reference surface, \( h \) is the deviation with respect to \( r \), and \( \rho \) is the surface roughness (\( \rho = 0 \) corresponds to a flat surface). The discrete surface height distribution, \( f_{h_d} \), is based on the Gaussian distribution in Eq. (3), but takes discrete steps:

\[ f_{h_d} = \frac{1}{b-a} \int_a^b \frac{e^{-(h-r)^2/(2\rho^2)}}{\rho\sqrt{2\pi}} dh, \quad \text{for } a \leq h < b \]

\[ = \frac{erf\left(\frac{b-r}{\sqrt{2\rho}}\right) - erf\left(\frac{a-r}{\sqrt{2\rho}}\right)}{2(b-a)}, \quad \text{for } a \leq h < b \]  

Fig. 5 shows both the continuous and discrete surface height distributions, with roughness \( \rho = 0.3 \) nm. For the discrete surface height distribution, the step size, i.e. \( (b-a) \), is 0.3 nm.

Langevin dynamics

To account for the stochastic collision of the solvent with the nanoparticles, and therefore Brownian motion, we used Langevin dynamics. In this method, a friction force and noise term are added to the equations of motion:
Figure 5: Continuous and discrete surface height distributions, with $\rho = 0.3$ nm. In the discrete case, the step size corresponds to 0.3 nm.

\[
\frac{dx(t)}{dt} = v(t) \quad (10)
\]
\[
m\frac{dv(t)}{dt} = -\zeta v(t) - \frac{dU}{dt} + F(t) \quad (11)
\]

where $x$ and $v$ are the position and velocity of a nanoparticle, $m$ is its mass, $\zeta$ is the friction coefficient, $U$ is the interaction energy between particles, and $F(t)$ is the stochastic noise term. This noise term fulfills $\langle F(t) \rangle = 0$ and $\langle F(t_1)F(t_2) \rangle = \Gamma(t_1 - t_2)$, where $\Gamma = 2\zeta k_B T$ quantifies the strength of the stochastic noise. We used the LAMMPS implementation of the thermostat proposed by Bussi and coworkers. In order to verify the accuracy of the integration, we used the effective energy conservation defined as:

\[
\tilde{H} = E_{tot} - \Delta E_{tstat} \quad (12)
\]

where $E_{tot}$ is the total energy of the system, and $\Delta E_{tstat}$ is the increment in energy due to the thermostat. We monitored the effective energy conservation for different values of timestep and damping parameters (see Fig. 6), for the smooth potential of particles with $\sigma = 60$nm, which corresponds to the steepest and strongest attractive potential. We find
effective energy conservation for $\Delta t = 5 \times 10^{-6}$, in a range of damping parameters 1-100 $\tau_{\text{water}}$.

**Calculation of fractal dimension**

We show an example of the box counting algorithm, for the percolating gel shown in Fig. 3C in the main document. The system is divided in $N_b = 1, 2, 3 \ldots$ segments on each dimension, and the number of filled boxes is counted. The log-scale plot of the number of filled boxes $N_f$ as a function of $L/l$ gives the fractal dimension, which is probed on the ranges of $l = [1\sigma, 5\sigma]$ for the local fractal dimension, and $l = [5\sigma, L]$ for the global fractal dimension.
Figure 7: Number of filled boxes as a function of the inverse of the box length normalized by the simulation cell size $L$, for the percolating cluster at $\phi = 0.10$ and $\rho = 0$ (shown in the main document as the structure in Fig. 3C. The global fractal dimension is calculated with the slope in the range $l = [5\sigma, L]$ and the local fractal dimension is calculated with the slope in the range $l = [1\sigma, 5\sigma]$. 

$\text{Global } d_f = 2.82$

$\text{Local } d_f = 1.57$
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