

Fractal Substructure of a Nanopowder

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(Received 22 February 2008; published 29 May 2008)

The structural evolution of a nanopowder by repeated dispersion and settling can lead to characteristic fractal substructures. This is shown by numerical simulations of a two-dimensional model agglomerate of adhesive rigid particles. The agglomerate is cut into fragments of a characteristic size ℓ , which then are settling under gravity. Repeating this procedure converges to a loosely packed structure, the properties of which are investigated: (a) The final packing density is independent of the initialization, (b) the short-range correlation function is independent of the fragment size, (c) the structure is fractal up to the fragmentation scale ℓ with a fractal dimension close to 1.7, and (d) the relaxation time increases linearly with ℓ .

DOI: 10.1103/PhysRevLett.100.218002

PACS numbers: 45.70.-n, 45.70.Qj, 61.43.Gt, 61.43.Hv

The van der Waals attraction between nanoparticles is much stronger than their weight. This is the reason why they agglomerate into ramified, often fractal structures [1]. A well-studied example are the agglomerates formed in a filter that collects nanoparticles. Once the particle deposits have grown to micrometer size, they can be shaken off the filter fibers easily. Collecting these rather large aerosol flakes in a container leads to what is commonly called a nanopowder, a fragile assembly of partly sintered micrometer flakes made of nanoparticles. Depending on the agglomeration process in the aerosol, as well as the influence of diffusion on the deposition process, the nanopowder will have fractal substructures [2]. However, it may be questioned whether these are robust: Shaking, pouring, stirring, and all kinds of random treatments of the container will break the nanopowder up into fragments, presumably with a typical size determined by the prevailing shear forces and much larger than the primary nanoparticles, but not necessarily larger than the originally collected aerosol flakes. When allowed to settle, these fragments will reaggregate, until the next perturbation breaks the nanopowder up again.

Nanopowders can be enormously porous. Porosities of more than 90% are common. Since many physical properties, such as electrical conductivity, mechanical stability, or catalytic activity are determined by the structure of the powder, it is important to know whether there emerge robust generic structural features as a result of repeated fragmentation and reagglomeration processes. In this Letter we present large-scale simulation results for a simple two-dimensional model which shows such a development of a robust asymptotic structure.

In our model the nanoparticles are represented by up to 3×10^6 discs with a narrow size distribution (10% variance). The initial state was a densely packed agglomerate. Below we will show that the final structure is independent of the initial configuration. Then the following procedure is

repeated many times: First the agglomerate is cut with a square mesh into portions. The linear mesh size ℓ can be viewed as the typical scale of the fragmentation process. A portion may consist of several disconnected fragments. These fragment flakes then settle as rigid bodies under gravity without taking adhesion forces with other particles into account. This is justified, if the flakes are sufficiently large, so that their weight exceeds the van der Waals force between the nanoparticles [3]. Brownian motion is neglected for the same reason. After this reassembly of the fragments the agglomerate is cut again with the square mesh, and so on; see Fig. 1.

The only model parameter is the linear mesh size ℓ . Note that the limit of small ℓ ($\ell \approx$ particle diameter) corre-

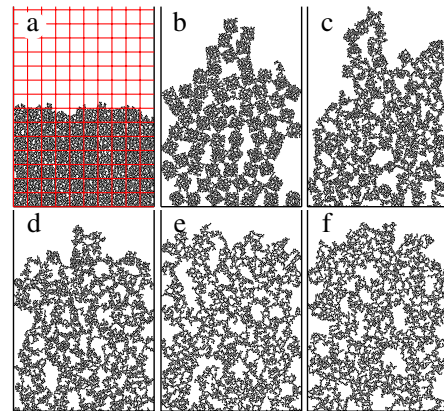


FIG. 1 (color online). Evolution of the packing of a nanopowder as described in the text. (a) Initial packing generated by random sequential sedimentation [4]. The packing is cut by a square mesh into fragments ($\ell = 20$); (b) The fragments are considered as rigid bodies and deposited (1st generation). Again the packing is cut by the square mesh (here not shown); (c) the fragments are deposited again (2nd generation), and so on; (d) 3rd generation; (e) 4th generation; (f) 120th generation.

sponds to noncohesive primary particles. In any case, the cohesion forces are assumed to be weak compared to the fragment weight, but strong enough to assure the internal stability of the flakes.

Algorithm.—To obtain statistically significant results for the structure of nanopowders one has to consider systems with more than 1×10^6 particles for many fragmentation-reagglomeration cycles. This is beyond the capability of molecular dynamics simulations. For our purpose we therefore generalized a model by Visscher and Bolsterli [4] originally intended for the sequential deposition of macroscopic spherical particles (see [5–9] for other applications): Each particle starts at a random position well above the already deposited material (the configuration of which is regarded as frozen in). Following gravity, it moves downwards until it touches the bottom of the container, where it sticks, or contacts another already deposited particle. In the latter case it moves, again following gravity, on the surface of the deposit until it either touches the bottom or finds a stable position in contact with the walls and/or previously deposited particles (for more details see [10]).

We generalized this algorithm in order to apply it to the fragments of a nanopowder. In each iteration step we inspect the portions which are cut out by the square lattice, Fig. 1, with respect to their connectivity. A portion may decompose into several fragments (i.e., clusters of connected nanoparticles). We deposit these fragments in a random sequence in the same way as described above. A fragment rolls down the surface of the deposit until the vertical projection of its center of mass falls in between two points of contact. As in the original algorithm, inertia is neglected, which in contrast to previous applications is less of a problem here, because the dynamics of nanoparticle flakes is usually strongly damped. In the following, lengths are given in units of the average particle radius, masses in units of the particle mass, and time as number of fragmentation-reagglomeration cycles.

Asymptotic filling height.—The original Visscher-Bolsterli algorithm produces random dense packings of spheres without fractal substructures. Correspondingly, our generalization produces a packing of fragments that is homogeneous on scales larger than the fragmentation length ℓ , as can be seen in Fig. 1(f). Surprisingly, however, the short-range structure up to size ℓ develops robust fractal properties. A first indication is given by the ℓ dependence of the filling height.

Starting from a random dense packing of primary particles the filling height increases towards a saturation value. Asymptotically, the powder adopts a very porous, statistically invariant structure, which is robust with respect to fragmentation at a fixed scale and subsequent gravitational settling of the fragments. Remarkably, the asymptotic filling height does not depend on the initial configuration: Starting with all particles arranged in a single vertical needlelike chain leads to the same value (see Fig. 2). Except for the first point (the initial condition) the filling

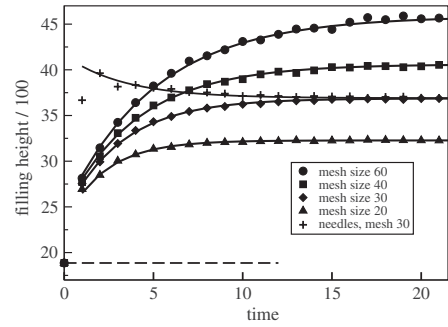


FIG. 2. Time evolution of filling height starting from a random dense packing of height h_0 (indicated by the dashed line). The same asymptotic filling height is reached from above, if the particles initially form a single vertical needle (data marked by +) instead of a random dense packing. The full lines are fits according to Eq. (1).

height h_n at iteration step n can be fitted by an exponential approach of the asymptotic height h_∞ with a relaxation time n_c ,

$$h_n = h_\infty(\ell) - (h_\infty(\ell) - h_0) \exp[-n/n_c(\ell)]. \quad (1)$$

The inset of Fig. 3 shows that

$$n_c(\ell) \propto \ell^z \quad \text{with} \quad z = 1. \quad (2)$$

For the asymptotic filling height, a power law

$$h_\infty(\ell) \propto \ell^\alpha \quad \text{with} \quad \alpha = 0.327 \quad (3)$$

gives a very good fit (see Fig. 3).

This implies that the number of portions cut from the steady-state configuration of a system of width L scales like $N_p = h_\infty L / \ell^2 \propto \ell^{\alpha-2}$. Consequently, the mass per portion is $M/N_p \propto \ell^{d_f}$ with

$$d_f = 2 - \alpha = 1.67 \pm 0.03. \quad (4)$$

One can interpret d_f as the fractal dimension of the structure on length scales smaller than the fragmentation length ℓ , because the short-range part of the pair correlation function $g(r)$ does not depend on ℓ (see Fig. 4). This means

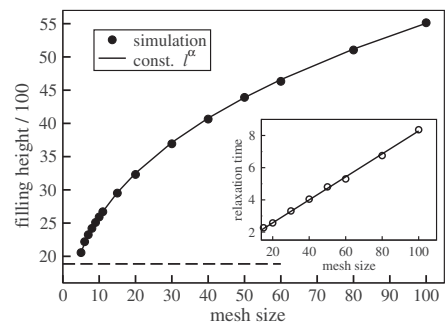


FIG. 3. The asymptotic filling height h_∞ grows as a power law $h_\infty(\ell) \sim \ell^\alpha$ with mesh size ℓ . The full line shows the best fit, $\alpha = 0.327$. Inset: The relaxation time $n_c(\ell)$ increases linearly with mesh size.

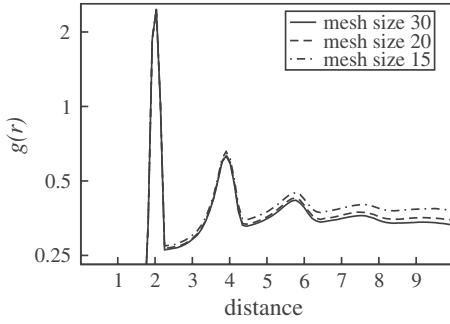


FIG. 4. Pair correlation function (semi-log-plot) of the steady state structure.

that the short-range structure is independent of the overall density. For large distances, on the other hand, the pair correlation function approaches the overall density, which decreases with increasing ℓ .

On first glance, however, the fractal dimension Eq. (4) seems at odds with the fact that the asymptotic average fragment mass grows linearly with the mesh size ℓ (Fig. 5), suggesting, instead, that the fragments are effectively one-dimensional structures. This puzzle can be resolved only by assuming that the number of disconnected fragments N_f per mesh cell has itself a power-law dependence on ℓ :

$$\frac{N_f}{N_p} \propto \ell^\beta. \quad (5)$$

As we are going to prove in a moment, the fragmentation-reagglomeration dynamics implies that the exponents β and d_f must be related by

$$\beta = d_f - 1. \quad (6)$$

Consequently the mass per fragment is linear in ℓ :

$$\frac{M}{N_f} \propto \frac{\ell^{d_f}}{\ell^\beta} \propto \ell. \quad (7)$$

The proof of the scaling relation Eq. (6) is based on the steady state condition that the deposition of fragments reestablishes on average as many contacts as were cut in the preceding fragmentation step. An $\ell \times \ell$ - mesh cell contains $\propto \ell^{d_f}$ particles, of which $\propto \ell^{d_f-1}$ are at the cell

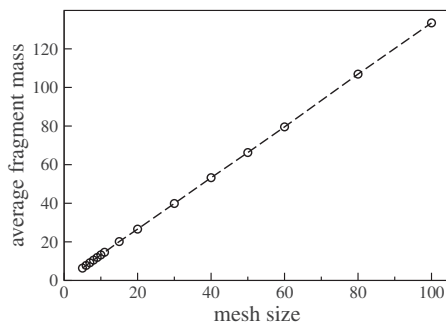


FIG. 5. Average fragment mass as a function of the mesh size ℓ in the asymptotic steady state.

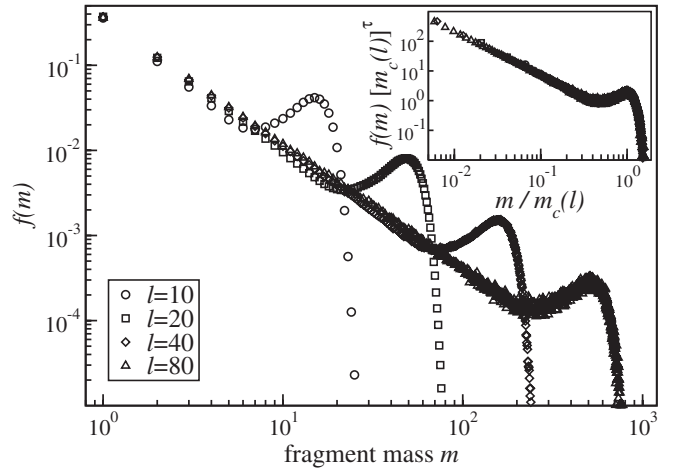


FIG. 6. Normalized fragment mass distribution for different mesh sizes ℓ . $f(m)$ is the number of fragments of mass m divided by the total number of fragments for a given ℓ . Inset: Data collapse using $m_c \propto \ell^{d_f}$ with $d_f = 1.695$ and $\tau = 1.41$.

boundary. Hence, the number of particle contacts cut by the boundary of one cell scales as

$$N_{\text{cut}} \propto \ell^{d_f-1}. \quad (8)$$

Each of the ℓ^β fragments forms two new contacts when deposited. Equating $N_{\text{cut}} = 2N_f/N_p$ gives Eq. (6).

Fragment mass distribution.—A detailed understanding of the fragment properties is provided by the distribution of fragment masses, shown in Fig. 6. It reveals that one must distinguish two types of fragments, large chunks at the upper end of the mass spectrum with a characteristic size m_c , and scale invariant dust responsible for the power-law part that is cut off by m_c . Comparing the mass distributions for different mesh sizes ℓ shows, that they can approximately be written in the form

$$f(m, \ell) = m^{-\tau} \tilde{f}\left(\frac{m}{m_c(\ell)}\right), \quad (9)$$

where the scaling function $\tilde{f}(x)$ is constant for $x \ll 1$, goes through a maximum at $x = 1$, and has an approximately Gaussian tail for $x \gg 1$. The typical mass m_c of the chunks

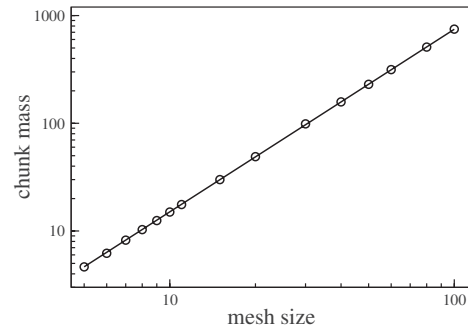
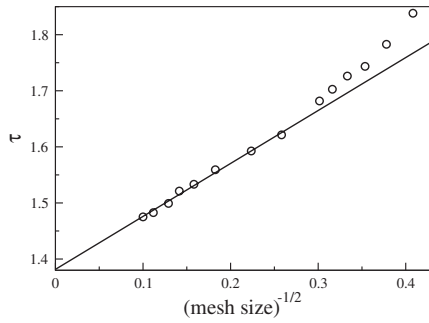


FIG. 7. Chunk mass m_c as a function of mesh size. Slope of straight line is 1.695.

FIG. 8. Effective dust exponent τ vs $1/\ell$.

has a power-law dependence on the mesh size, $m_c = 0.304\ell^{1.695}$ (Fig. 7), the exponent being in good agreement with the value of d_f , Eq. (4).

The evaluation of the dust exponent, τ , is more difficult, since the slope fitted to the power law part of the mass distribution in the log-log-plot Fig. 6 decreases significantly with increasing ℓ . An extrapolation of τ for $\ell^{-1/2} \rightarrow 0$, see Fig. 8, gives an estimate of $\tau \approx 1.38$. However, an independent method of determining τ gives a larger value. It is based on the important observation that the width of the chunk distribution is proportional to m_c . Hence the fraction of chunks among the fragments vanishes like

$$f_{\text{chunks}} \propto m_c^{1-\tau} \propto \ell^{d_f(1-\tau)}, \quad (10)$$

because τ is larger than 1. Hence, the normalization of $f(m)$ for $\ell \rightarrow \infty$ implies that

$$1 = f(1) \sum_m m^{-\tau} = f(1) \zeta(\tau) \quad (11)$$

with Riemann's zeta function at the argument τ . Solving this equation numerically with $f(1) \approx 0.36$ (for the ℓ values we considered) gives an estimate $\tau \approx 1.46$.

We have seen that the overwhelming number of fragments are dust particles, apart from a vanishing fraction of chunks. However, these dust particles carry only a vanishing fraction of the total mass M . According to Eq. (7),

$$m_{\text{dust}} \leq f(1) \zeta(\tau - 1) \frac{N_f}{M} \propto \frac{1}{\ell} \quad (12)$$

vanishes for $\ell \rightarrow \infty$. Essentially all the mass is in the few chunks. This explains why the mass (essentially mass of chunks) per fragment (essentially per dust particle) (Fig. 5) has nothing to do with the fractal dimension.

Now a consistent picture has formed: Each portion (or mesh cell) contains typically one chunk. The number of fragments per portion, which according to Eq. (5) scales like ℓ^β , can thus be identified with $1/f_{\text{chunks}}$, which according to Eq. (10) scales as $\ell^{d_f(\tau-1)}$. This shows that the fractal dimension of the chunks and the dust exponent are not independent of each other. Using Eq. (6) they obey the

scaling relation

$$d_f(2 - \tau) = 1. \quad (13)$$

For $d_f = 1.695$ this implies $\tau = 1.41$, in between the two τ values obtained above. These values lead to an excellent data collapse for the fragment mass distributions [see Fig. 6 (inset)].

This investigation offers several interesting directions to be explored further. In particular the modeling of the fragmentation process using a rigid square mesh (a "sieve") seems a bit contrived for nanopowders. It is responsible for cutting off the tiny fragments we called dust along the boundaries of the mesh cells. Other fragmentation processes like shaking or stirring are likely to produce less dust. Whether or not they lead to a broader or a narrower chunk size distribution remains an open question. Last, but not least, the extension of the model to three dimensions will probably change the exponents.

We would like to thank I. Goldhirsch for fruitful discussions. This work was supported by the German-Israeli Foundation by Grant No. I-795-166.10/2003.

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