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Introduction

Understanding the interaction of nanomaterials with their surrounding is the focus of a rising multi-disciplinary research effort. This has become a main priority as both energy generation by hydrocarbon combustion and the development of scalable nano-fabrication processes are rapidly increasing the anthropogenic production and emission of nanostructures. The ultra-fine component of these emissions (< 100 nm) is sufficiently small to penetrate the cardiovascular system upon uptake in the lungs and induce oxidative stress with a resulting dysfunction of lung endothelial cells.¹ This underlies the development of various diseases² with epidemiological studies showing a correlation between environmental particulate air pollution and a range of endpoints of lung morbidity and mortality.^{3,4} In addition, the commercial production of high performing nanomaterial-based devices such as high-storage capacity batteries, sensors and solar cells requires scalable fabrication processes. A major challenge is to develop methods that

Self-assembly dynamics and accumulation mechanisms of ultra-fine nanoparticles†

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The self-assembly of nanomaterials into three-dimensional hierarchical structures is a fundamental step impacting a large number of synthetic and natural processes. These range from the scalable fabrication of nano-devices such as batteries, sensors and third generation solar cells to the uptake and accumulation of particulate pollution in the lung alveoli. Here, we show that the Dynamic behavior of ultra-fine particles (UFP < 100 nm) diverges significantly from that of sub- and micro equivalents. For freely diffusing bodies, this leads to the formation of stochastically reproducible films that approach the morphology and density of ballistically deposited ones. A novel deposition mechanism and regime are proposed that successfully capture the full spectrum of size-dependent self-assembly dynamics. These findings are a significant step toward the engineering of scalable parallel nano-fabrication approaches, and the understanding of the interaction of unbound nanostructures with their surrounding.

enable robust integration of zero-, one- and three-dimensional nanomaterials with sub-micrometre accuracy and control.

Amongst scalable self-assembly routes, gas-phase nucleation/clustering and aerosol deposition are at the core of indusnanomaterial production. Several nanostructured trial commodities such as carbon black, titania pigments and fumed silica are produced in megatons per year by flame synthesis.⁵ Collision and coalescence of bodies in the gas-phase is a widespread process^{6,7} that controls the self-assembly of matter from initial atoms⁸ to molecular clusters⁹ and their rapid growth into nano- and micro-scale particles.^{10,11} Collision and dwell conditions govern the resulting body density and morphology. Non- and poorly-coalescing bodies undergoing Brownian collision, for example, can rapidly form fractal-like structures such as soot,^{12,13} deemed a main agent in environmentally induced lung cancer^{14–16} and carbon-black, a key material in tire and ink production. Synthesis of three-dimensional nanostructures has been demonstrated by deposition of diffusing nanoparticles. This is a scalable low-cost route for the wafer-level parallel fabrication of high performing nano-devices^{17,18} with potential for emerging technologies such as third-harmonic-upconversion antennas.¹⁹ However, the limitations and commercial potential of aerosol-based approaches is ultimately determined by the ability to controll the accumulation and self-assembly dynamics of nanomaterials on a surface.²⁰

The dynamics of nanomaterials in the gas phase is usually described in terms of the ratio between the constant displacement induced by an advective velocity and the stochasticallydistributed one induced by Brownian motion, namely the Péclet number (Pe). Several studies^{21–23} have proposed that the resulting key structural properties and morphologies are

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determined by this ratio alone and are independent of the depositing body size. For example, spherical particles of 5 and 500 nm colliding with a solid surface at a constant Péclet number are expected to lead to the self-assembly of films with the same morphology. However, recent findings^{24,25} have questioned the validity of these models and underlying assumptions. Numerical solutions to the Langevin's equation of motion have shown an up to 500% increase in film density for deposition of 5 nm spherical particles in the diffusion regime. Similar discrepancies from the Péclet-scaling law were observed by direct Monte Carlo simulations for deposition of 10 nm spheres. As interfacial phenomena are determinant factors in the interaction of nanomaterials with their surroundings,26 an improved understanding of nanostructure deposition and accumulation has a significant potential impact on our health and nano-fabrication capabilities.

Here, the dynamics of unbound particles is investigated over three orders of magnitude in size aiming to determine a comprehensive mechanistic description of their accumulation and self-assembly behaviors. Particle displacement is computed by large-scale, grid-free numerical solutions of the Langevin's equation of motion from the ballistic to the diffusion regime. Validation of the resulting morphologies is pursued by aerosol deposition of freely diffusing nanoparticles and topographical mapping by atomic force and scanning electron microscopes. A novel deposition regime that combines features of ballistic- and diffusion-driven dynamics is proposed. This enables the quantitative predictions of micro- to nanoparticle interaction with their surroundings providing a unified model of their diverging self-assembly mechanisms.

Results and discussion

Initially, conditions were determined to capture the multiscale porosities and hierarchical film structures resulting from the directed (ballistic regime) and undirected (diffusion regime) self-assembly of nanoparticles²⁰ (Fig. S1 and S2[†]). With this aim, the dynamics of monodisperse spheres with a diameter (d_p) of 50 nm was simulated by grid-free solution of the Langevin equation of motion as previously discussed in detail.²⁷ Domain independent properties were obtained by asymptotic convergence of the film morphologies with increasing deposition surface/domain size (Fig. S2 and S3[†]). Validation of these numerical results was done by a comparison of the converged nanoparticle solid fraction with previous largescale Monte Carlo simulations (Table 1). These showed a good agreement and a characteristic S-shaped dependency on the Péclet number in line with very recent results²⁸ (Fig. S4[†]). It was found that small deposition surfaces having a square side $(L_{\rm d})$ smaller than 120 times the particle diameter lead up to 59% artificially higher film densities (ESI, section III⁺). This is attributed to the physical constrains that are not sufficient to achieve periodic symmetry conditions and thus, do not enable the establishment of the multi-scale nano- and micro-porosity observed by aerosol deposition of nanoparticles and agglomerates.²⁹ This explains the drastic increase in film densities (*ca*. 500%) predicted in the diffusion regime for deposition of ultra-fine nanoparticles ($d_p < 30$ nm) by recent small-domainconstrained studies.^{21,25} As a result, all further simulations were conducted with a large domain size of $140d_p$ that enables the self-assembly of more realistic, hierarchical film morphologies.

Self-assembly dynamics of nanoparticle films

To determine the effect of the nanoparticle size on the film self-assembly dynamics, the structural properties obtained by deposition of 50 and 5 nm particles were further investigated. Fig. 1 shows sections of the hierarchical morphologies formed by self-assembly in the diffusion and ballistic regimes. Each contiguous set of touching particles, a surface-formed and bond agglomerate, was labeled with a color. It was found that independent of the deposition regime and particle size, nanoparticle film self-assembly is driven by the formation of parallel agglomerates growing in the vertical direction (Fig. 1). However, the density and horizontal spreading of these

Table 1	Comparison of film	structural parame	eters obtained by pa	article deposition dynamics

	Particle diameter	Peclet-number	Domain length	Film thickness	Deposition surface	Average film porosity ($\varepsilon_{ m avg}$)
This work	50 nm 30 nm 10 nm	10 ⁻⁷ -100	140 <i>d</i> _p	120 <i>d</i> _p	Flat square	0.990-0.867 0.988-0.867 0.973-0.861
Elmøe <i>et al.</i> ²⁷ Rodríguez <i>et al.</i> ²³ Mädler <i>et al.</i> ²⁵	5 nm 50 nm <i>a^a</i> 30 nm 10 nm 5 nm	$\begin{array}{c} 10^{-2} - 10 \\ 10^{-1} - 100 \\ 10^{-7} - 100 \end{array}$	$\frac{200d_{\rm p}}{512d_{\rm p}}$ $\frac{30d_{\rm p}}{}$	$180d_{ m p} \\ 400d_{ m p} \\ 160d_{ m p}$	Cylindrical capillary walls Flat square Flat square	$\begin{array}{c} 0.957 - 0.859 \\ 0.98 - 0.86^{b} \\ 0.98 - 0.86^{b} \\ 0.965 - 0.84 \\ 0.925 - 0.84 \\ 0.90 - 0.84 \end{array}$
Kulkarni <i>et al.</i> ²¹ Dreyer <i>et al.</i> ²⁴ Castillo <i>et al.</i> ²⁸	30 nm 30 nm 10 nm a^a	Diffusion & ballistic regime Diffusion regime 10 ⁻¹ –100	$30d_{ m p}\ 30d_{ m p}\ 512d_{ m p}$	$50d_{\rm p}$ $100d_{\rm p}$	Flat square Flat square Flat square	$\begin{array}{c} 0.969 - 0.848^{b} \\ 0.93 \\ 0.98 - 0.86^{b} \end{array}$

^{*a*} The domain was structured in a cubic subdomain lattice with a side length of *a*. ^{*b*} The average porosity was estimated from the plateau packing density (Φ_{sl}).

agglomerates was strongly dependent on the particle size and deposition conditions leading to significantly different morphologies and structural properties.

For the 50 nm particles, two distinct characteristic accumulation behaviours were determined. In the diffusion regime, the film morphology was characterized (Fig. 1a) by the rapid establishment of a prevailing agglomerate in the first $10d_p$ of thickness. These large structures shadowed the deposition surface collecting the incoming nanoparticle flux. At $20d_p$ thickness, a single agglomerate became prevalent spreading over a horizontal surface of $10d_p \times 10d_p$. Further increasing the film thickness did not result in additional horizontal growth but in a series of laterally-confined agglomerates growing in parallel. This branch-like vertical growth is in line with the morphology observed for aerosol-deposited TiO₂³⁰ and SnO₂³¹ nanoparticle films utilized as porous dye sensitized solar cell electrodes and chemical sensors, respectively. In contrast, ballistically-driven deposition led to a different film structure (Fig. 1d). There, it was not possible to identify a prevailing agglomerates. Instead, several parallel agglomerate grew from the deposition surface. This is attributed to the relatively small path swept by each depositing particle at high Péclet numbers and in line with the high film density observed by deposition of nanoparticle aerosols in Berner low-pressure impactors.³²

In contrast, the 5 nm particles did not feature these two opposite structural regimes. Instead, in the first $10d_p$ film thickness, both diffusion- (Fig. 1b) and ballistic-driven (Fig. 1e) growth revealed the same structural densities and morphologies as those observed for the 50 nm particles in the ballistic regime (Fig. 1d). Above $40d_p$ thickness (Fig. 1c), diffusion-driven deposition of 5 nm particles led to the establishment of a single surface-bond agglomerate morphology. This is in line with the initial densification computed with decreasing particle size at low Péclet numbers (Fig. 2). Further-



Fig. 1 Three dimensional plots of film sections self-assembled in the diffusion (a, b, c) and ballistic (d, e) regimes for particles 50 nm (a, d) and 5 nm (b, c, e) in diameter. Each contiguous set of particles (surface-bond agglomerate) was labeled with a color.



Fig. 2 Representative slice packing density profiles (a) in the ballistic and (b) diffusion regimes as a function of the particle diameter from 50 to 5 nm. Three main density maxima (a, b, insets) are determined at 0.8, 1.6, and 2.4 relative film thicknesses (z/d_p) . The magnitude of these maxima is (a) independent of the particle diameter in the ballistic regime while (b) increases by more than 100% with decreasing particle size in the diffusion regime.

more, it shows that the self-assembly dynamics of ultra-fine spheres having a diameter below 50 nm differ from that expected for purely diffusive bodies and, close to the substrate surface, approaches ballistic-induced self-assembly. This is attributed to a self-induced variation of the collision mechanism with decreasing particle size leading to similar vertically-directed straight collision trajectories as for ballistic bodies. These findings explain the high density observed for thin nanoparticle patterns obtained by electrodynamics focusing of charged particle-laden aerosols.¹⁷

Particle size-dependent structural properties

The correlation between film structural properties and particle size was further investigated by computation of the film density profiles (Fig. 2) as a function of the particle diameters in the ballistic (Pe = 100) and diffusion regimes (Pe = 10^{-7}). It was found that in the former all particle sizes lead to identical packing density profiles (Fig. 2a). In contrast, in the diffusion regime the surface density of the first particle layer increases by more than 100% with decreasing particle diameter from 50 to 5 nm (Fig. 2b). Furthermore, film growth did not lead to the establishment of a constant/plateau-density as for ballisticdriven self-assembly (Fig. 2a). Instead, for diffusion-driven deposition, the density decreased continuously from an initial maximum near the substrate interface to a minimum on the top film surface. This is particularly relevant with respect to the accumulation of ambient UFP in the lung alveoli and the nano-fabrication of three-dimensional nanostructured layers as in both systems particle deposition is, usually, diffusiondriven. The high and variable density of the nanoparticlesubstrate interface, reported here, indicates that the established Péclet-scaling laws cannot be applied to model the interaction and accumulation of diffusive nanoparticles with their surroundings.

Further investigation of the nanoparticle film morphologies revealed a unique structure. For both the ballistic and diffusion regimes, a ripple-like density profile (Fig. 2a and b, insets) was observed in the first $10d_p$ film thickness. This was characterized by three main peaks representing the maxima and minima of the local slice densities. The first density peak was located at $0.8d_p$ height from the deposition surface and, for ballistic deposition (Fig. 2a, inset), reached the highest slice packing density of 0.3 and thus nearly half of the random close packing density (0.64) for monodispersed spheres. This is attributed to the discrete dimension of the depositing nanoparticles. In fact, for deposition of a single layer of spheres on a flat surface, the maximal density would always be found at a film height of $0.5d_p$. Here, the shift from $0.5d_p$ to $0.8d_p$ height is attributed to the intercalation of the second layer during three-dimensional growth.

The second and third density peaks (Fig. 2a and b, insets) were found to be consistent at $1.6d_p$ and $2.4d_p$ thicknesses and attributed to the second and third particle layer maxima. Further, smaller peaks were found at alternating film heights above $2.4d_p$ but their position and intensity did not converge among different simulations resulting in a destructive interference. This suggests that at a thickness of $2.4d_{\rm p}$, the film morphology evolves from a two- to a three-dimensional disordered state. However, while for ballistically driven deposition the peaks' magnitude was independent of the particle size (Fig. 2a, inset), in the diffusion regime (Fig. 2b, inset) it increased with decreasing particle diameter. The first peak $(0.8d_p)$ slice packing density increased from 0.122 to 0.239 with decreasing particle size from 50 to 5 nm. As a result, a 5 nm nanoparticle film had an initially 100% higher density than that made of 50 nm particles. This significant densification of the substrate-nanoparticle interface explains the rapid shunting of ultra-sensitive chemical sensors made by aerosol

deposition of *ca*. 5 nm particle layers.¹⁸ Furthermore, it indicates that the mechanisms governing the accumulation of particles on an interface change with decreasing size. This leads to a significantly denser substrate–nanoparticle interface than that previously modeled with sub-micro and micro-scale particles in the diffusion regime.²³

The validity of these predictions was assessed by characterization of the interface morphology obtained by deposition of particle-laden aerosols on polished Si-wafers. A hot TiO2 aerosol with an average particle diameter of 5 nm and a narrow size distribution was produced by flame synthesis of organometallic precursors as previously reported in detail.³³ This aerosol was orthogonally impinged on a polished Si-wafer resulting in a thermophoretically-driven³⁴ particle flux directed toward the wafer surface. The aerosol concentration and deposition conditions were controlled by the precursor concentration, dilution and temperature gradient²⁰ resulting in nearly non-agglomerated nanoparticles as determined by thermophoretic sampling on TEM grids (Fig. S5[†]) and deposition at Péclet numbers of 10^{-1} – 10^{-2} (as computed in the ESI, section II[†]). It was found that by sufficiently decreasing the deposition time, a quasi-monolayer of particles in contact with the substrate surface could be self-assembled.

Fig. 3a shows an atomic force microscopy (AFM) topographical scan of the Si-wafer surface upon deposition of a complete first layer of nanoparticles. The surface was characterized by a nano-scale roughness with most peaks having an average height of *ca*. 5 nm in good agreement with the TiO₂ particle size. Some few peaks with a maximal height of *ca*. 17 nm were randomly distributed on the surface and are attributed to the

initial formation of surface-bond agglomerates. Particle deposition and initial film self-assembly were confirmed by scanning electron microscopy (SEM) analysis (Fig. 3b). Simulation of 5 nm particle deposition under comparable conditions (Pe = 10^{-2}) and with a maximal film thickness corresponding to that measured by AFM (17 nm) led to similar structural morphologies (Fig. 3c). These were also characterized by a rough matt of 5 nm asperities with some few higher peaks randomly spread on the surface. The impact of the temperature difference between the simulations and the flame-made aerosol deposition experiments was accounted by the computation of the Péclet number that results in the same diffusion coefficient and the advection velocity ratio. The larger mean free path of the experimental particles is expected to lead to only slightly higher interface densities as the ratio between the mean free path and particle size is close to one for both experimental and simulated particles.

A comparison of the film side view obtained by AFM and particle dynamics (Fig. 3a, insets) showed consistent crosssections with, however, smoother film height variations observed by AFM. This was attributed to the limited AFM inter-particle resolution not enabling to resolve small gaps between the deposited particles. Doubling the aerosol exposure time nearly doubled the film thickness (Fig. 3d) leading to a maximal film height of nearly 35 nm. This is in line with the constant film growth rates reported for thermophoretic deposition of flame-made nanoparticle aerosols.²⁰ This confirms further that upon deposition of the first nanoparticle monolayer (Fig. 3a and b) the film growth proceeds mainly by self-assembly of parallel agglomerates vertically-aligned to the deposition surface (Fig. 3b and c).



Fig. 3 AFM topography and SEM images of (a, b) a quasi-monolayer and (d, e) a multi-layer of TiO_2 nanoparticles (5 nm in diameter) aerosol-deposited on polished Si-wafers. The AFM and SEM analyses revealed a consistent surface density (SD) of 0.2 ± 0.015 . Comparison of 5 nm particle size distributions computed by Langevin dynamics shows comparable cross-sectional (a, b, insets) and (c, f) horizontal morphological features.

This morphology was equivalent to that obtained by simulation of 5 nm nanoparticle deposition with a maximal film thickness of 35 nm (Fig. 3d, inset). A main difference between the simulated (Fig. 3c and f) and aerosol-deposited films was the larger variation in size observed by SEM (Fig. 3b and e). This is attributed to both the polydisperse nature of the flame-made nanoparticles, and the limited resolution of the SEM not being able to discern primary particles of 5 nm within single agglomerates. Analysis of the nanoparticle surface by AFM and SEM revealed a surface density (SD) of 0.20 \pm 0.015 and thus very close to that (0.19 \pm 0.003) predicted by particle dynamics.

Self-assembly mechanisms and regimes

The mechanisms underlying this interface densification and diverging self-assembly dynamics were assessed by analysis of the surface density (Fig. 4) over a comprehensive range of deposition conditions. Independent of the particle size, all density profiles had an S-shaped dependence from the Péclet number (Fig. 4a) and converged toward a density of 0.25 in the ballistic regime. However, at low Péclet numbers, the surface density was a function of the particle size. There, decreasing the particle size from 50 to 5 nm increased the surface density from 0.11 to 0.19. This is in very good agreement with the AFM- and SEM-surface densities (0.20 ± 0.015) obtained by aerosol deposition of 5 nm particles at a Péclet number of 10^{-2} – 10^{-1} (Fig. 3a).

Here, it is proposed that the increase in the surface density with decreasing particle size is due to a decrease in the horizontal area swept by the particle during its transition through the collision length. The latter can be computed by the minimal vertical collision distance from a particle deposited in the first layer and for monodisperse particles is equal to $d_{\rm p}$.

Although in the diffusion regime both small (*e.g.* 5 nm) and large (\geq 50 nm) particles are expected to deposit by a random

path, this is not always true within a small collision distance (Fig. 4b, insets). In particular, if the collision length (d_p) is smaller than the particle mean free path (λ_p) the particle can move on a straight trajectory before collision with the surface. This results in a decrease of the horizontal area swept by the particle and therefore of its collision likelihood. As a result, more ultra-fine particles can reach the deposition surface resulting in the higher interface density computed with decreasing particle size (Fig. 4a).

This accumulation mechanism was validated by the development of a comprehensive analytical model for the surface density (Fig. 4a, lines). As detailed in the ESI (Fig. S6†), the average surface density was estimated by the ratio between the horizontal projections of the area occupied by a deposited sphere (A_{d_p}) and that swept $(A_{\text{stat}} + K_{\text{RPF}} \times A_{\text{dyn}})$ through the collision length (d_p) :

$$SD = \frac{A_{d_{p}}}{A_{stat} + K_{RPF} \times A_{dyn}}$$
(1)

with A_{d_p} being the horizontal area $(\pi d_p^2/4)$ occupied by a deposited spherical particle, A_{stat} being the horizontal collision area (πd_p^2) of a depositing particle, A_{dyn} being the horizontal projection of the area swept by a particle moving at an incident angle α through the collision length, α being the angle between the vertical axis and the trajectory of a particle moving horizontally due to Brownian displacement (X) and vertically due to an advective velocity and Brownian displacement (vt + X), and K_{RPF} being the additional path swept by a particle due to the stochastic nature of diffusion. The horizontal projection of the area swept (A_{dyn}) is only a function of the particle size and Péclet number, and thus of the relative Brownian displacement ($\bar{X} = X/d_p$):

$$A_{\rm dyn} = 2d_{\rm p}^{\ 2}\overline{X} - d_{\rm p}^{\ 2} \left[\overline{X}\sqrt{1-\overline{X}^2} + \sin^{-1}(\overline{X})\right] \tag{2}$$



Fig. 4 Scaled particle surface density (SD) as a function (a) of the Péclet number and (b) particle mean free path to diameter ratio at $Pe = 10^{-7}$ for different particle sizes. Comparison of the surface density computed by (a, symbols) Langevin dynamics and (a, lines) modeled by eqn (3) with the corresponding K_{RPF} shows good agreement. Departure from the diffusion regime is observed (b) already for particles smaller than 100 nm.

This leads to a general analytical equation for the surface density with the only variables being the relative Brownian displacement and swept path (K_{RPF} factor):

$$SD = \frac{\pi}{4\left[\pi + K_{RPF}(2\overline{X} - \left[\overline{X}\sqrt{1 - \overline{X}^2} + \sin^{-1}(\overline{X})\right]\right]}$$
(3)

The validity of this analytical model (Fig. 4a, lines) was assessed against the surface density computed by particle dynamics simulation (Fig. 4a, symbols). For all particle sizes and Péclet numbers, eqn (3) shows an excellent agreement with the numerical results with minor deviations observed only in the transition regime (Pe = $10^{-1} - 1$). In the ballistic regime, the Brownian-induced displacement within the collision length approaches zero, resulting in $A_{dyn} \ll A_{stat}$, and thus to a converging surface density $\approx A_{d_p}/A_{stat} = 0.25$ (Fig. S6†). In contrast, at low Péclet numbers, the area swept by a depositing particle within the collision length increases, leading to $A_{dyn} \approx A_{stat}$, and thus, for the 50 nm particles, up to 50% less dense interface than in the ballistic regime (Fig. 4a).

It was found that the length of the swept path and thus the magnitude of the K_{RPF} factor decreased with decreasing particle size leading to more dense interfaces. This is attributed to the different deposition mechanisms. In fact, while purely diffusive particles (\geq 50 nm) perform a random trajectory within the collision length, sufficiently small particles can cross it on a straight line (Fig. S6[†]) due to their mean free path being larger than the collision length (particle diameter). However, such (straight) ballistic deposition behaviour differs from that in the ballistic regime, as the depositing particle trajectory is not orthogonal to the substrate but has an incident angle determined from the ratio between the vertical and horizontal displacement. The maximal incident angle (α_{max}) was found to be $Pe \ll 1$ and represents an orthogonal, nearly isosceles, triangle having as hypotenuse the particle trajectory (Fig. S6[†]). This regime, hereafter referred to as randomlyoriented ballistic regime, requires a larger area for a particle to be deposited than in the pure ballistic regime but a considerably smaller area than that of purely diffusive bodies. This is in good agreement with the observed film (Fig. 2b) and interface (Fig. 4a) densification with decreasing particle size.

The conditions for departure from the diffusion to the randomly-oriented ballistic deposition regime and their effect on the $K_{\rm RPF}$ factor were investigated for quasi-purely diffusing bodies (Pe of 10^{-7}). Fig. 4b shows the resulting interface density at a Péclet number of 10^{-7} as a function of the ratio between the particle mean free path (λ_p) and the collision length (d_p) and the particle size ranging from the micro-scale (1 µm) to the end of nano-scale (1 nm). The resulting surface density showed an S-shaped dependency from the λ_p/d_p ratio approaching 0.21 and 0.08 for 1 and 1000 nm particles, respectively. Most importantly, in the randomly-oriented ballistic limit the $K_{\rm RPF}$ factor converged toward 1. This is in excellent agreement with the proposed straight single-diagonal step deposition model and explains the different deposition mechanisms observed for small (< 100 nm) nanoparticles.

In contrast, for large sub- and micro-scale particles having a mean free path considerably smaller than their diameter a true random path is achieved throughout the collision length. This results in an increased swept path ($K_{\rm RPF}$) approaching 17 times that travelled by the smallest particles (Fig. 4b). These findings show that the dynamics of ultra-fine nanoparticles (< 100 nm) is not accurately captured by the diffusion regime, and their accumulation mechanism relies outside the validity of the established Péclet scaling laws. Furthermore, as the swept path does not depend only from the particle size but also on its ratio with the particle mean free path, with increasing surrounding temperature large nanoparticles will result in similar interface densifications as smaller ones.

Here, in contrast to previous studies,^{21,24,25} we have shown that the densification of films synthesized by self-assembly of diffusive ultra-fine particles does not involve the whole film structure but is confined to a certain thickness from the deposition surface. As a result, sufficiently thick films (> $80d_p$) converge toward the same density (Fig. 2b). This densification is attributed to the straight diagonal trajectory followed by sufficiently small (< 100 nm) ultra-fine particles within the collision length from the deposited particle layer. Also in contrast to previous reports, this densification was observed to become predominant already below 100 nm, and thus for the whole ultra-fine particle range. An S-shaped densification was observed with particle size varying from 1 µm to 1 nm identifying that the strongest morphology variation is expected between a particle size of 5 to 100 nm. Amongst other, this model is a significant step toward the large-scale fabrication of emerging nano-devices such as third-harmonic-upconversion antennas where ultra-fine semiconductor nanoparticles (< 25 nm) need to be precisely collocated in the small gap (e.g. 35 nm) of a plasmonic nanorod dimer.¹⁹ With respect to the self-assembly of polydisperse aerosols, often encountered in realistic conditions, two contrasting mechanisms are expected. Deposition of small particles on the surface of larger ones is known to increase the total film density by partially filling the pores between large particles. On the other side, if small particles are deposited on the deposition surface close to a, previously deposited, larger particles than the relative collision length would be increased resulting in a smaller mean free path to collision ratio. This would in turn decrease the film density close to the interface. As a result, the effect of polydispersity is not trivial and cannot be predicted independently of the specific size distribution, mean free path to average particle size ratio and film thickness.

Conclusions

A novel mechanistic description of the self-assembly mechanisms of nanoparticles into three-dimensional structures was presented. It was found that the structural properties of hierarchical films made of ultra-fine particles diverge from that

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expected in the diffusion regime for sub-micron and micro equivalents leading to up to 300% denser interface morphologies. A new randomly-oriented ballistic deposition regime was successfully proposed to account for the collision and densification mechanisms of nanostructures. This enabled a precise prediction of their accumulation and clustering dynamics by a simple analytical model that accounts for the degree of randomness of the deposition process.

In all regimes, the formation of surface-bond fractal-like agglomerates was determined as a main mechanism for the establishment of hierarchical morphologies. These findings are a significant step toward the understanding of the interaction of suspended nanostructures with their surroundings. This has an immediate effect on the engineering of several synthetic and natural nano-fabrication processes. For example, it elucidates the rapid achievement of electrical percolation in dispersed nanoelectrode devices, a bottleneck in improving the conductivity of nanoparticle films. It enables the modeling and engineering of the properties of nano-patterned structures by scalable means such as electrodynamics focusing. Furthermore, this model can be applied to the investigation of the inflammatory effects of ultrafine particles (UFP < 100 nm) on human lungs providing new insights into the interaction of nanomaterials with delicate biological interfaces.

Experimental

Particle dynamics is modeled for isothermal conditions at 298 K, considering the deposition of one particle at a time. In order to obtain true random motion before deposition, a particle is initially released into a cell where particle deposition and film growth are not allowed. The next particle is released after deposition of the previous one. Deposition occurs when a particle touches another particle or the horizontal surface at the end of the deposition domain using a sticking coefficient of 100%. Electrical charge, van der Waals force and extra intermolecular forces are neglected. More details about the model outline are reported elsewhere.²⁷

Flame spray pyrolysis (FSP) was used in combination with a water-cooled substrate holder for synthesis and direct deposition of pure TiO₂ polished Si-wafers. Nanoparticle aerosols were prepared as follows: titanium (IV)–isopropoxide (Sigma Aldrich, purity > 97%) was diluted in xylene (Fluka, purity > 98%) to obtain a metal-atom concentration of 0.02 mol l^{-1} . The solution was supplied at a rate of 5 ml min⁻¹ through a custom-build atomizer and dispersed into a fine spray with 5 l min⁻¹ oxygen at a pressure drop of 5 bar. The spray was ignited by a supporting ring-shaped premixed methane/oxygen flame (CH₄ = 1.2 l min⁻¹, O₂ = 3.2 l min⁻¹).

Nanoparticles were deposited by orthogonal impingement of the hot aerosol generated by FSP on the substrates placed at 20 cm height above the burner (HAB). The substrates were 1 mm thick Si-wafers with a deposition area of 1×1 cm². The aerosol temperature (T_F) in the proximity of the substrate was 773 K as measured by an n-type thermocouple placed upstream of the substrate, and it was in agreement with values reported for a similar FSP deposition setup.^{20,34} Surface topography was investigated in non-contact mode with an atomic force microscopy system (Cypher, Asylum Research). A commercial cantilever (Olympus AC240TM, Asylum Research) was used as a tip, which has a force constant of 2 N m⁻¹, a resonant frequency of 70 kHz, and a tip radius of ~28 nm. Scanning electron microscopy (SEM) and transmission electron microscopy analyses were conducted with a Zeiss Ultraplus (FESEM) operated at 3 kV and Hitachi H7100FA 125 kV, respectively. The first layer surface density (SD) was computed from the simulations, AFM and SEM images from the ratio of the projected area covered by the particles to the total surface area with the aid of a standard image processing software (ImageJ). All SD computations were repeated for eight different AFM/SEM images, and simulations to obtain statistically comparable average values.

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