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(54) **MODELING OF NANOPARTICLE
AGGLOMERATION AND POWDER BED
FORMATION IN MICROSCALE SELECTIVE
LASER SINTERING SYSTEMS**

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(2013.01); **B22F 2998/10** (2013.01)

(57) **ABSTRACT**

Exemplified microscale selective laser sintering (μ -SLS or micro-SLS) systems and methods facilitate modeling of the nanoparticle powder bed by simulating the interactions between particles during the powder spreading operation. In particular, the exemplified methods and system use multi-scale modeling techniques to accurately predict the formation and mechanical/electrical properties of parts produced by selective laser sintering of powder beds. Discrete element modeling is used for nanoscale particle interactions by implementing the different forces dominant at nanoscale. A heat transfer analysis is used to predict the sintering of individual particles in the powder beds in order to build up a complete structural model of the parts that are being produced by the SLS process.

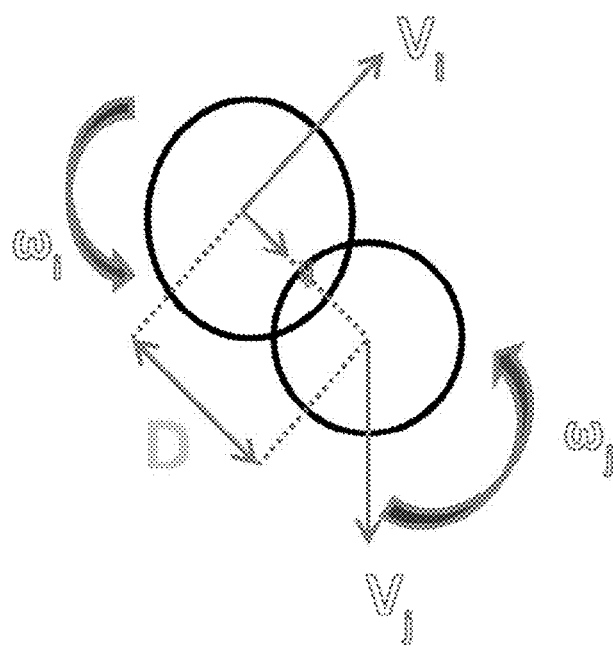


FIG. 1

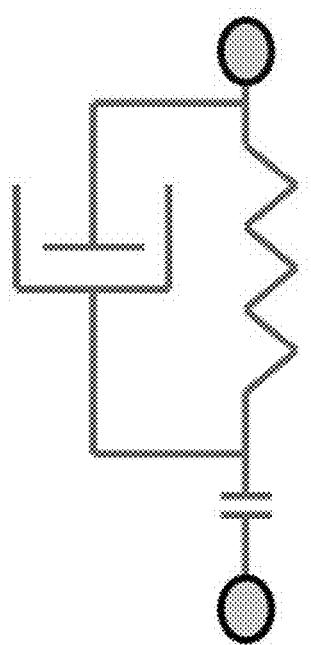


FIG. 2

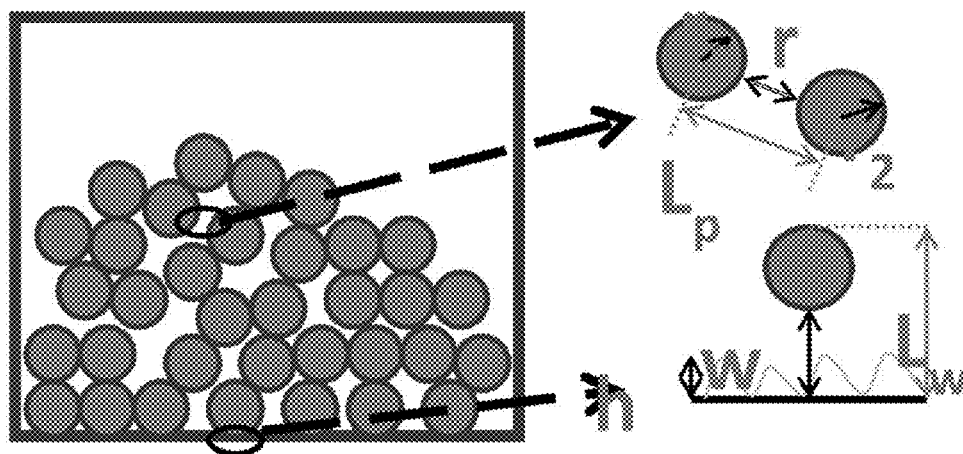


FIG. 3

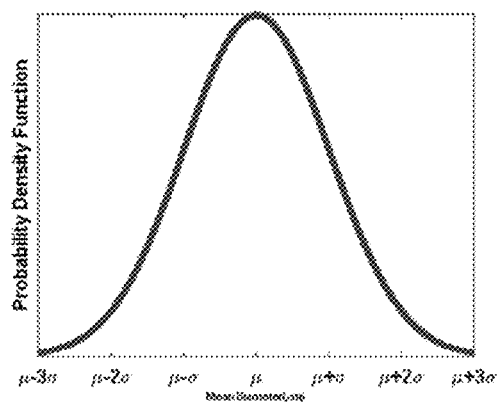


FIG. 4

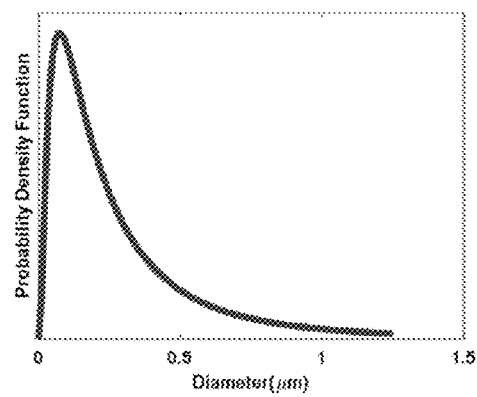


FIG. 5

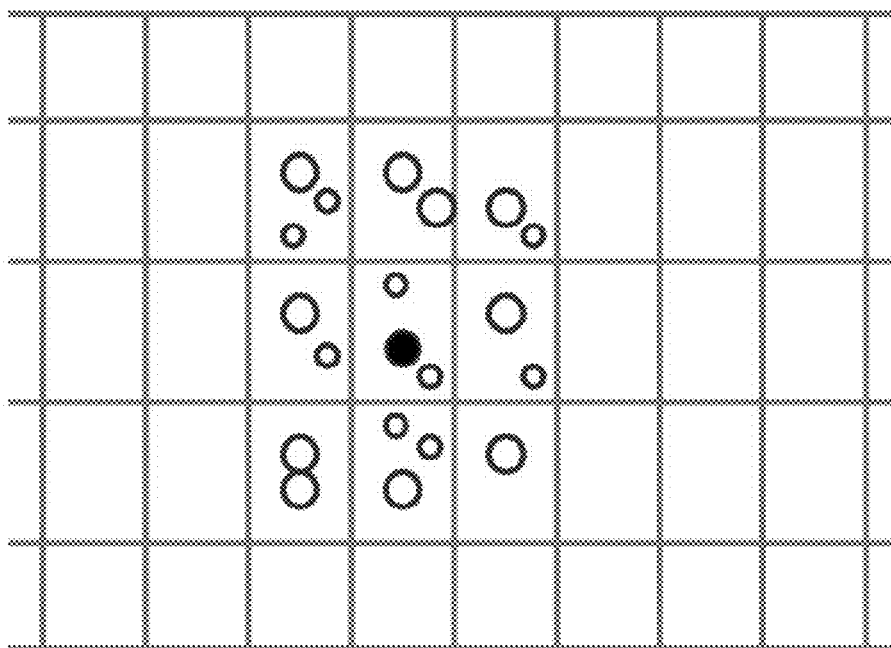


FIG. 6

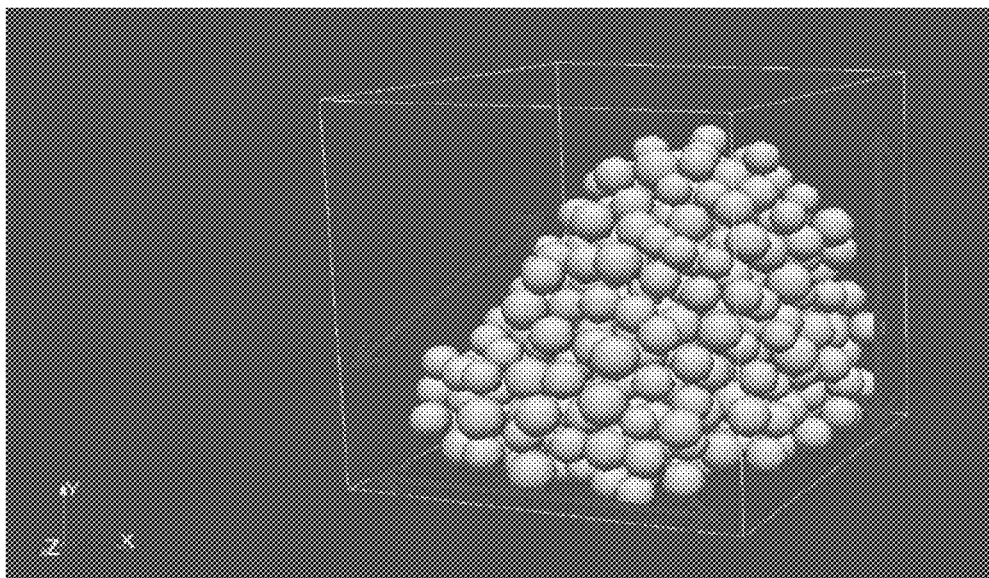


FIG. 7

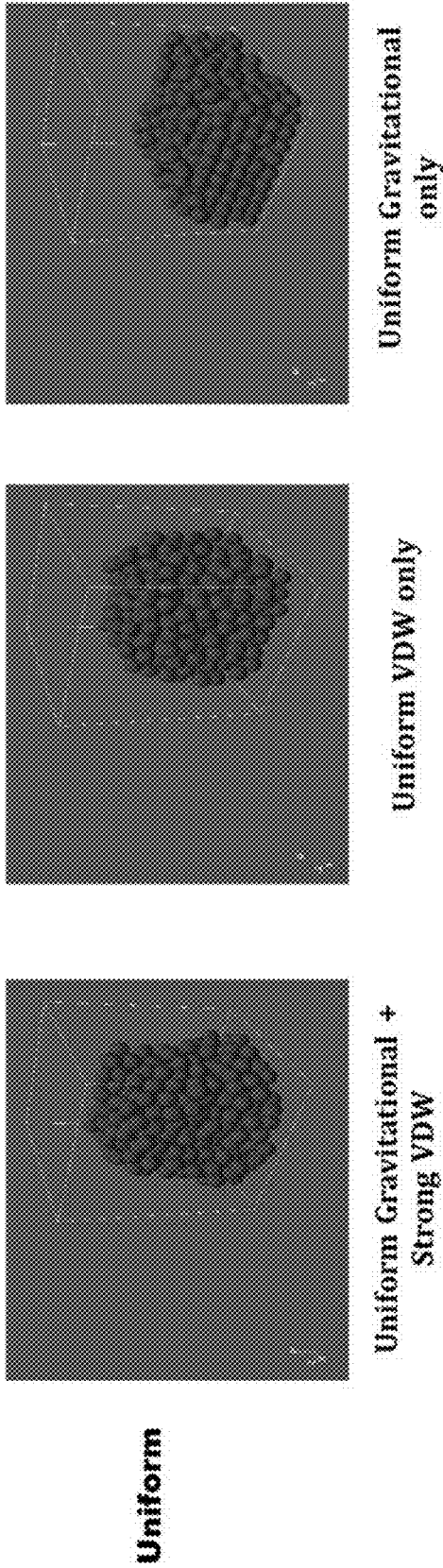


FIG. 8

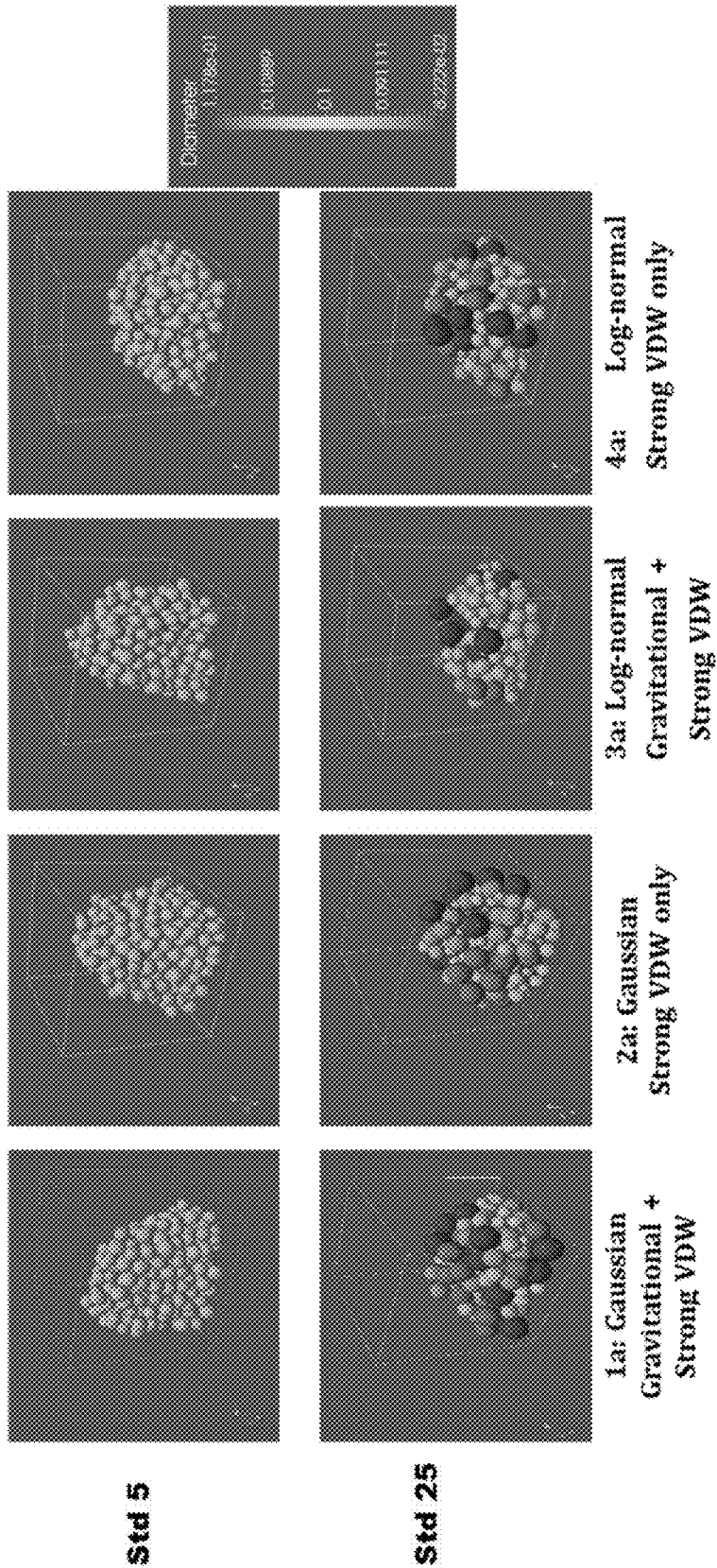


FIG. 9

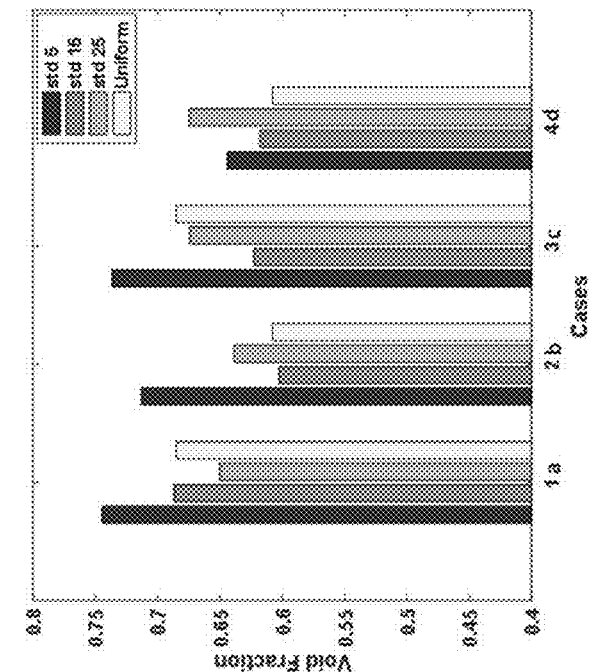


FIG. 10B

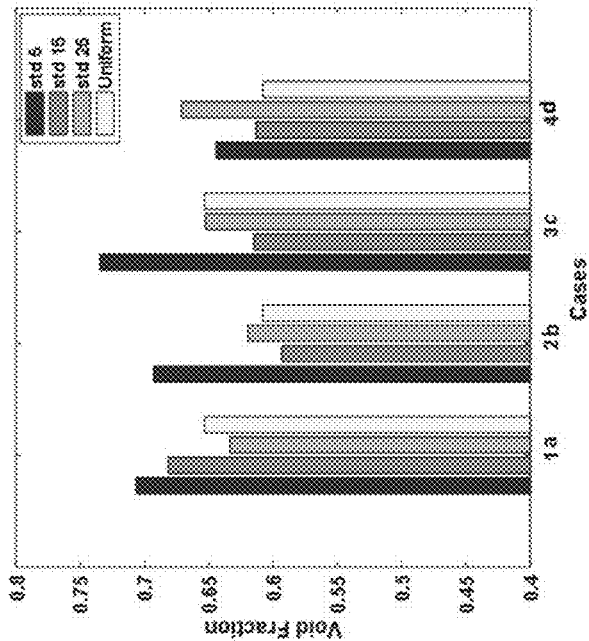
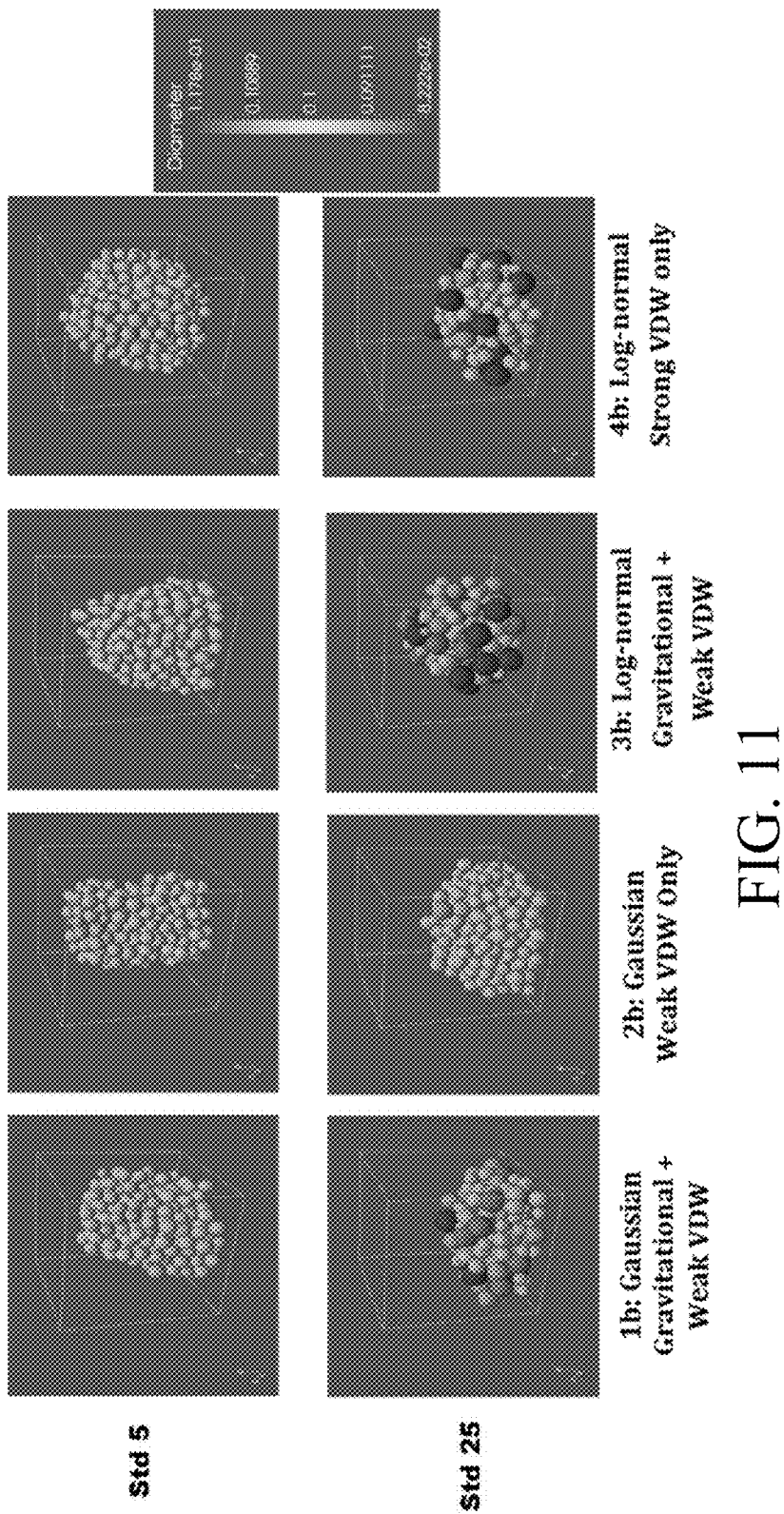


FIG. 10A



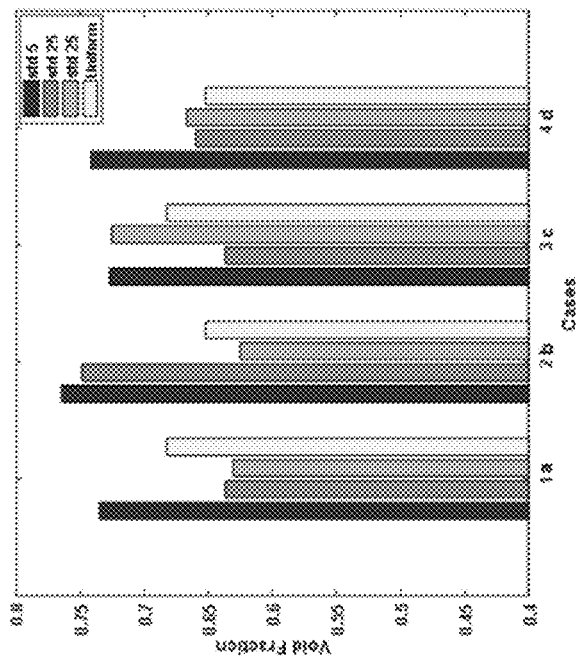


FIG. 12B

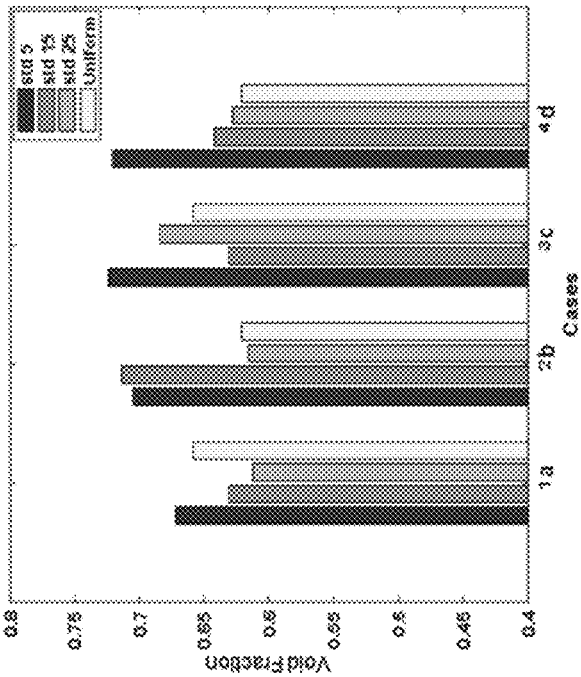
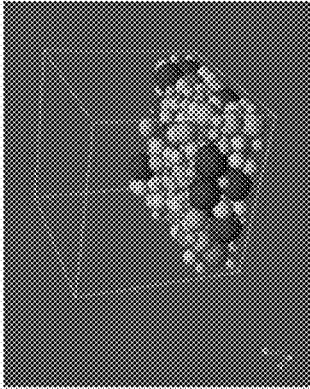
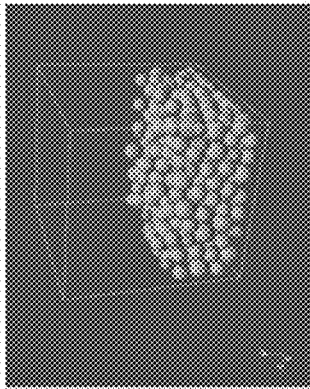
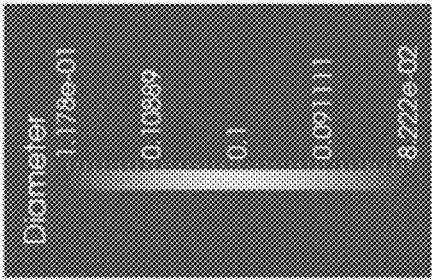
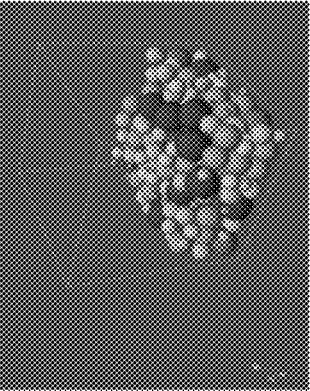
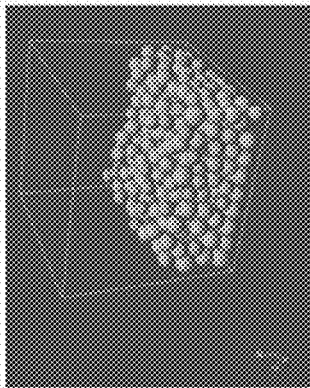


FIG. 12A



6: Log-normal
Gravitational Only



5: Gaussian Gravitational Only

Std 5

Std 25

FIG. 13

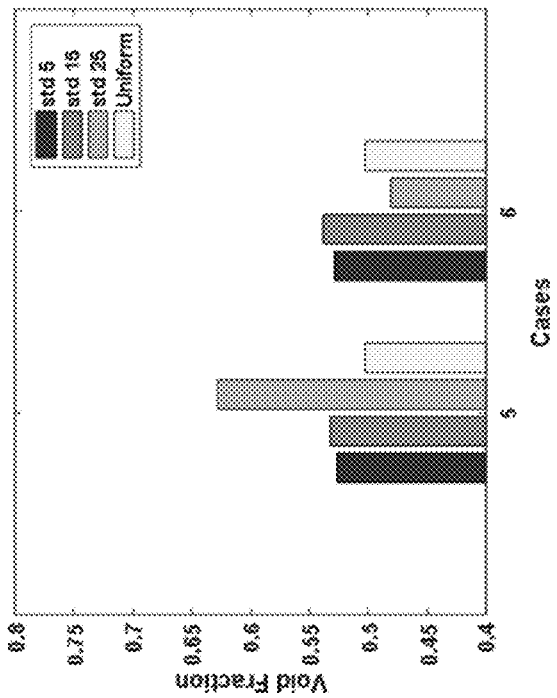


FIG. 14B

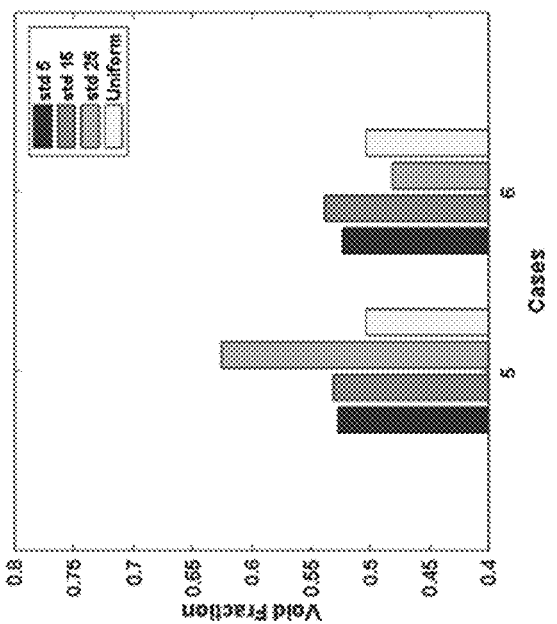


FIG. 14A

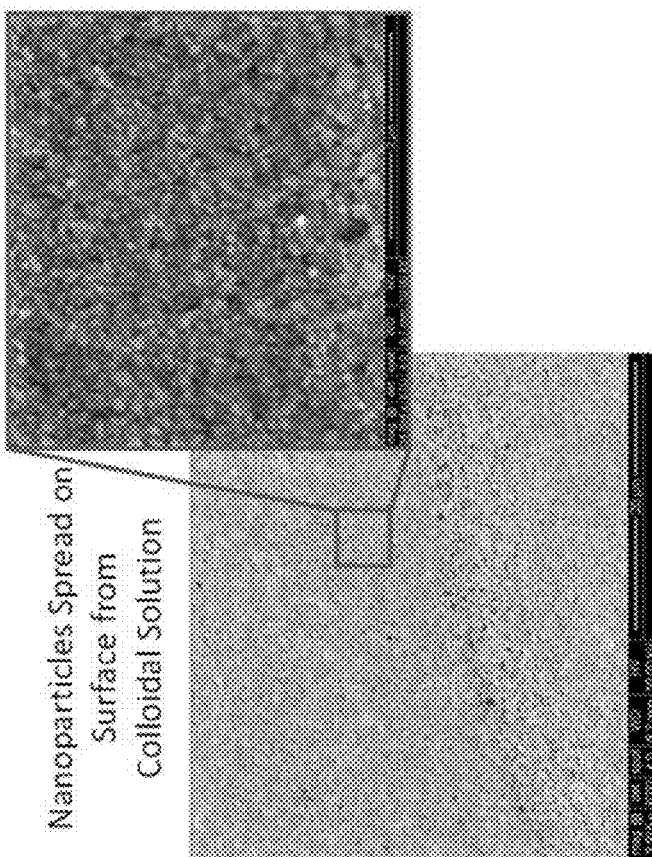


FIG. 15B

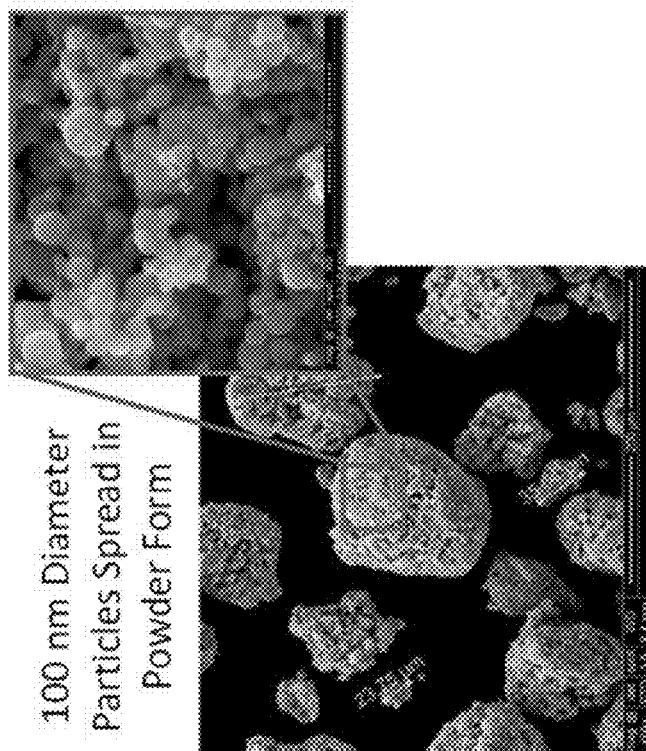


FIG. 15A

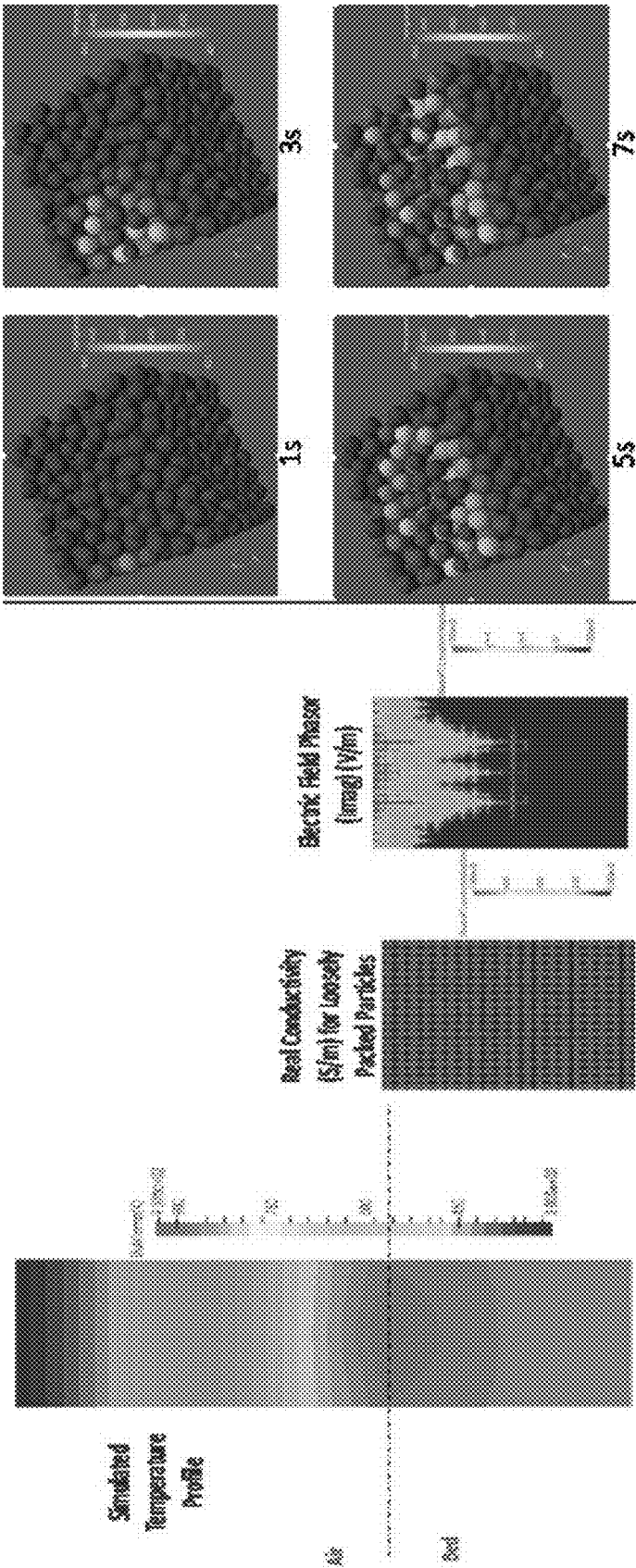


Fig. 16D

Fig. 16C

Fig. 16B

Fig. 16A

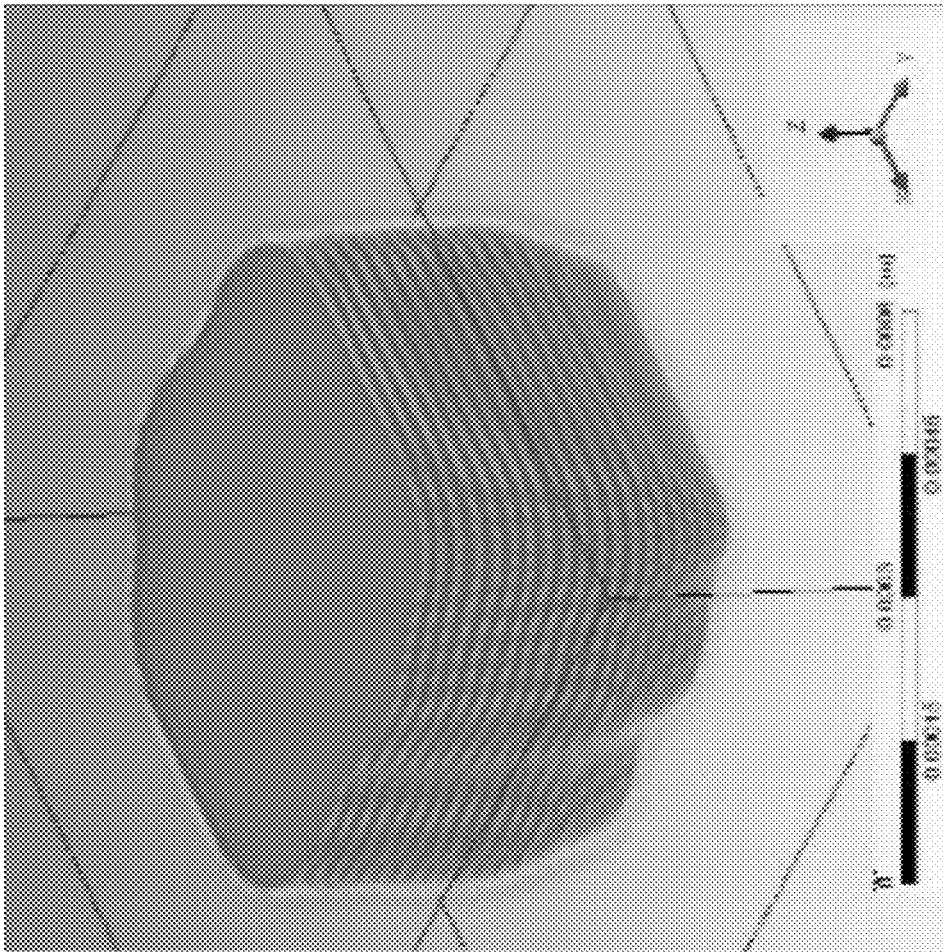


FIG. 17

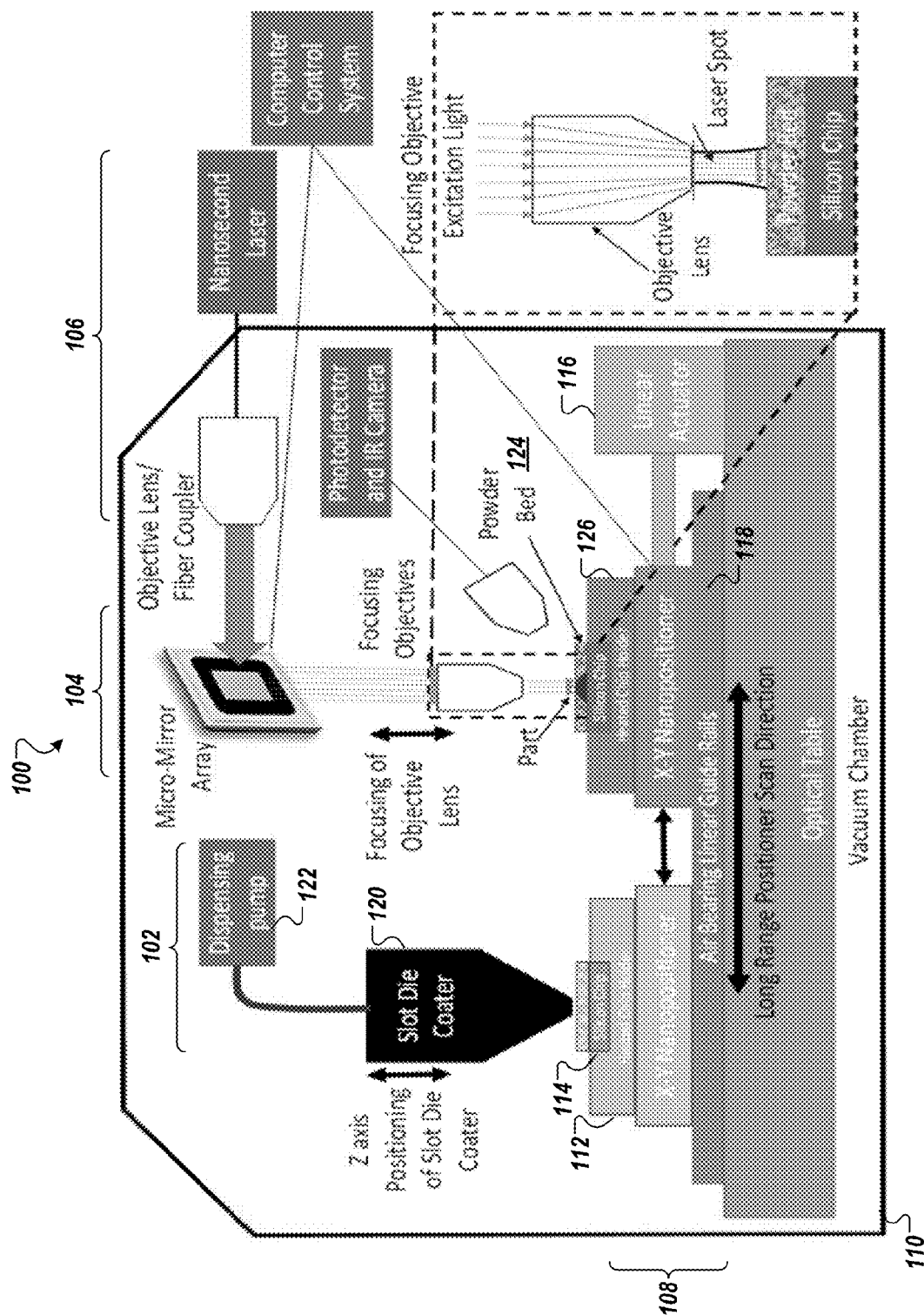
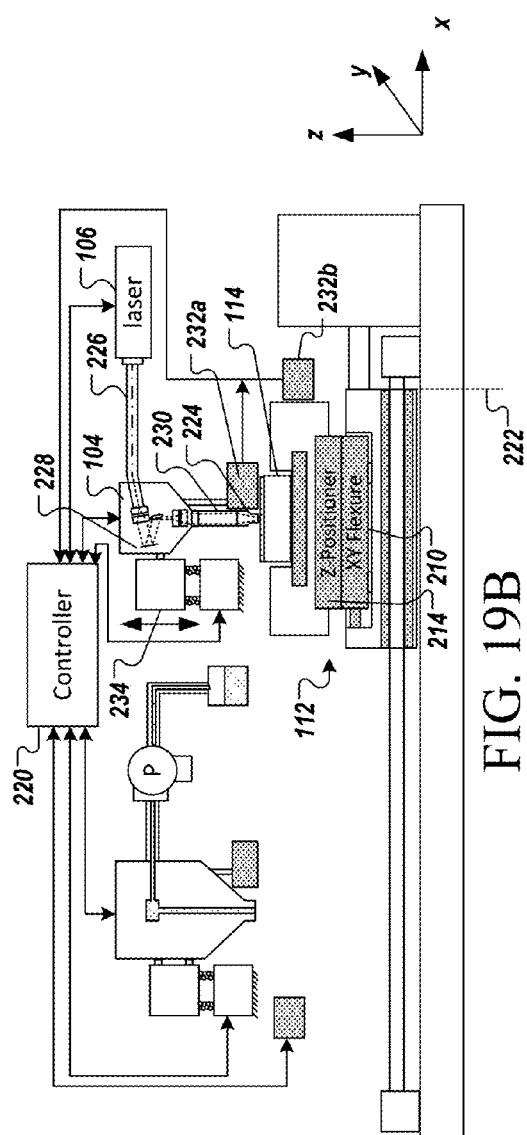
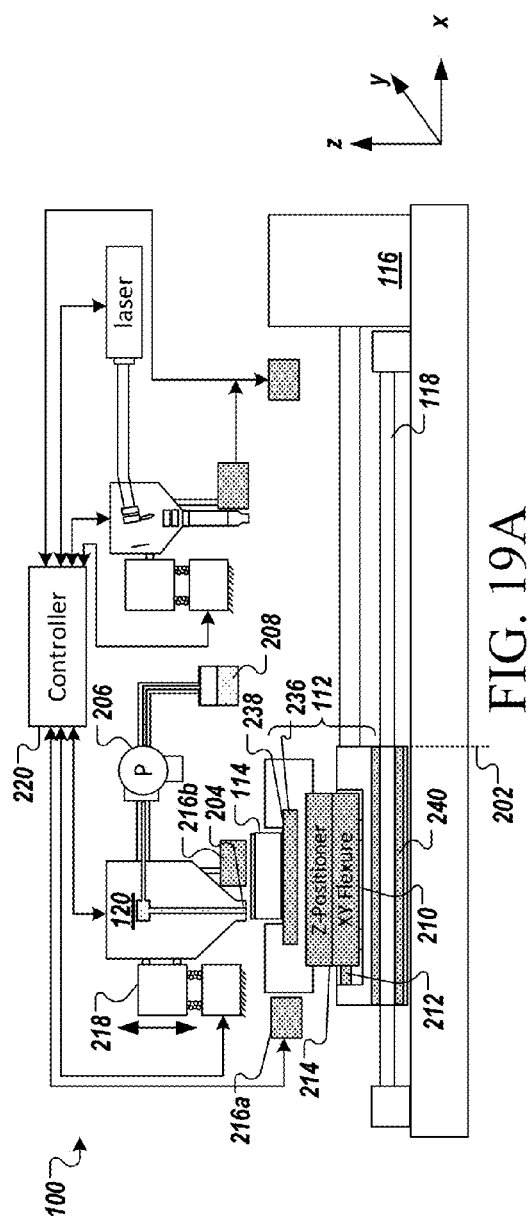


FIG. 18



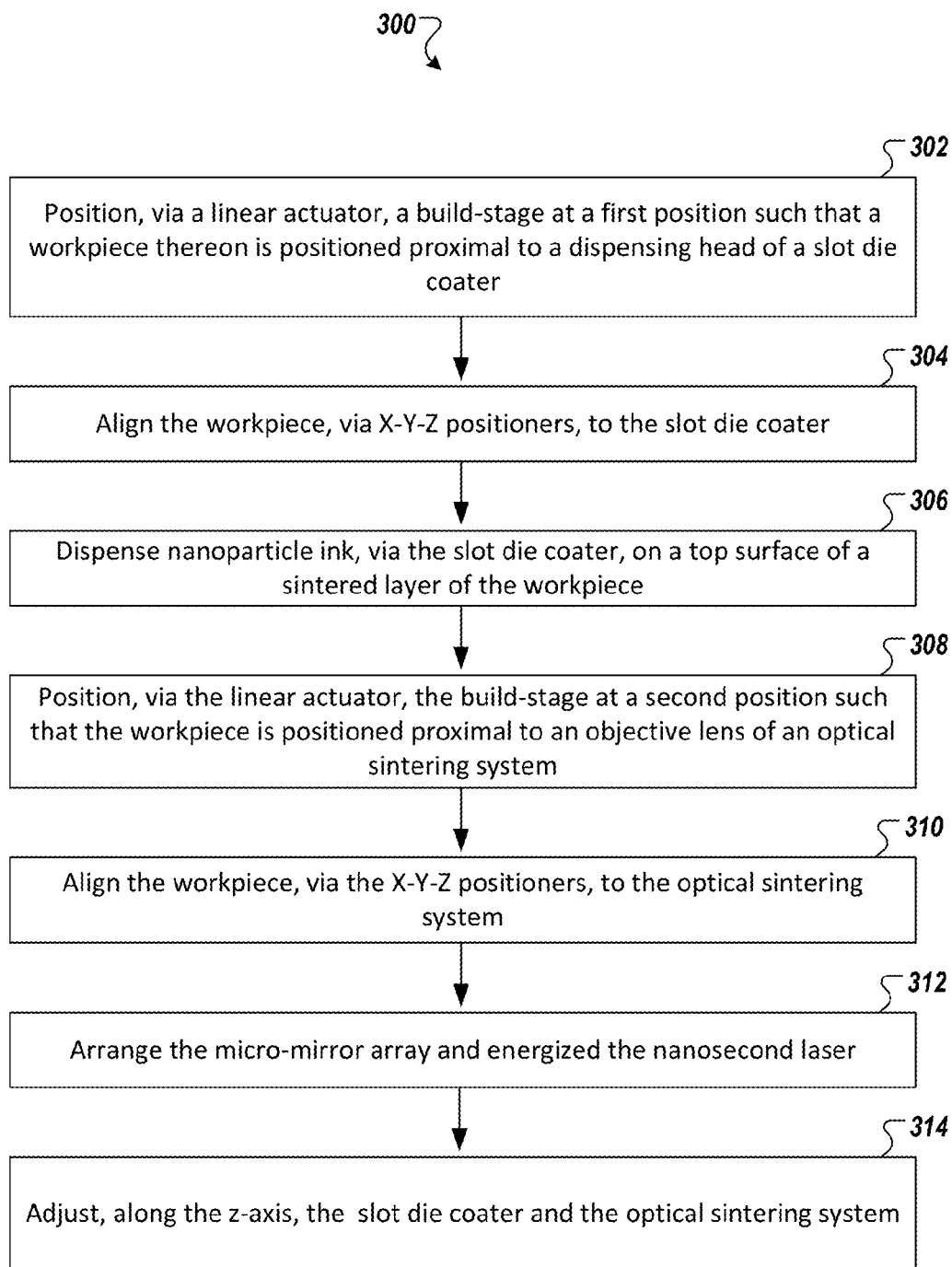


FIG. 20

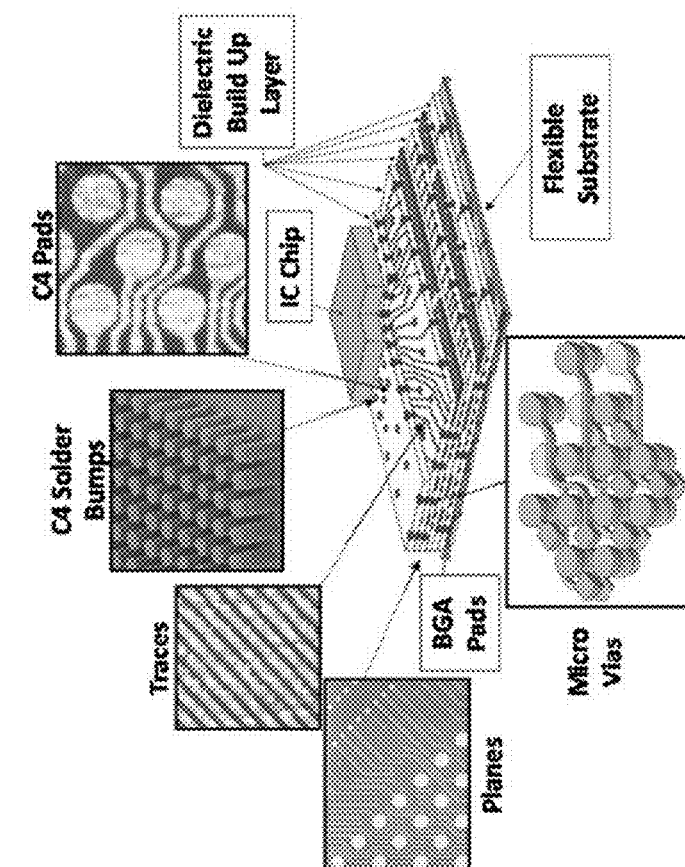
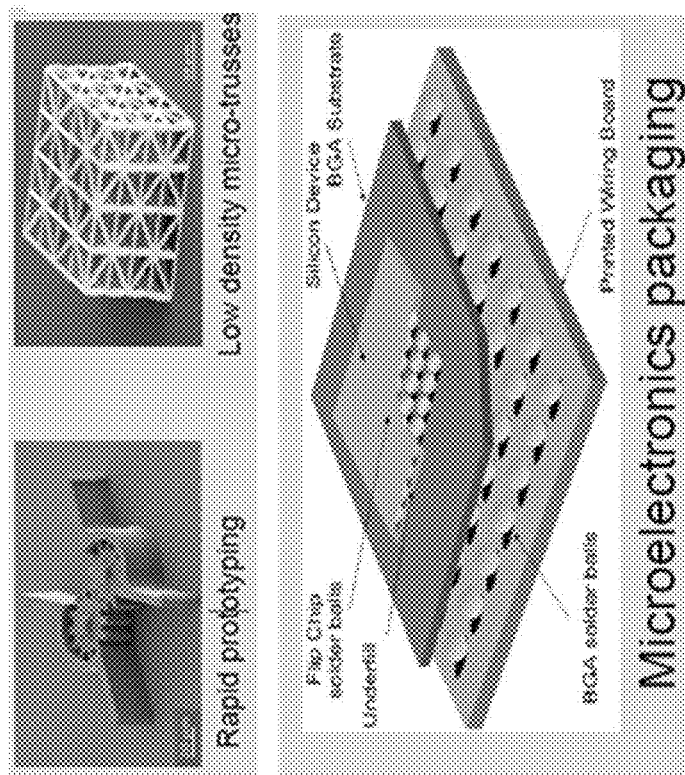


FIG. 21



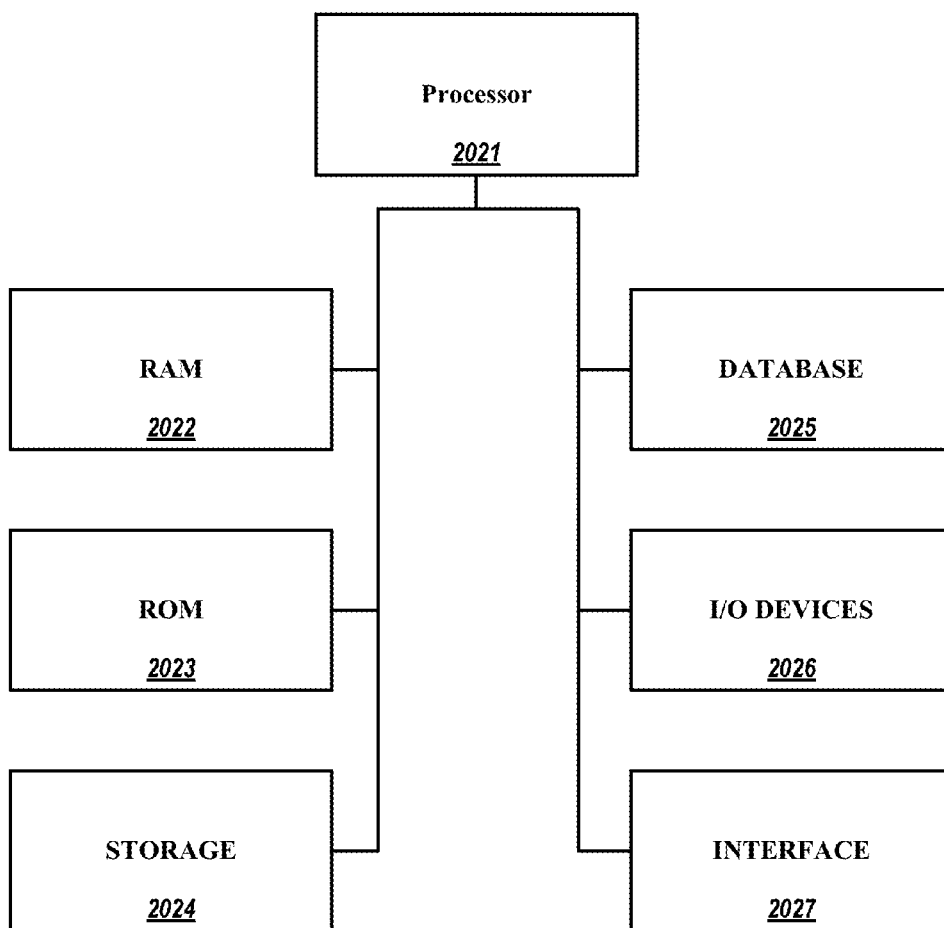


FIG. 22

MODELING OF NANOPARTICLE AGGLOMERATION AND POWDER BED FORMATION IN MICROSCALE SELECTIVE LASER SINTERING SYSTEMS

RELATED APPLICATIONS

[0001] This application claims priority to, and the benefit of, U.S. Provisional Appl. No. 62/316,644, filed Apr. 1, 2016, title “Micro-Selective Sintering Laser System and Method Thereof”; U.S. Provisional Appl. No. 62/316,666, filed Apr. 1, 2016, title “Modeling of Nanoparticle Agglomeration and Powder Bed Formation in Microscale Laser Sintering Systems”; and U.S. Provisional Appl. No. 62/454,456, filed Feb. 3, 2017, title “Micro-selective Sintering Laser on Flexible Substrates and With Multi-Material Capabilities,” each of which is incorporated by reference herein in its entirety.

BACKGROUND

[0002] Micro- and nano-scale additive manufacturing methods in metals, plastics, and ceramics have many applications in the aerospace, medical device, and electronics industries. For example, the fabrication of additively-manufactured parts with micron-scale resolutions makes possible the production of cellular materials with controlled microstructures. Such materials can exhibit very high strength-to-weight ratios, which is critical for a number of applications in the aerospace industry. Similarly, the medical industry could benefit from the additive manufacturing of metal parts with controlled microstructures, since this process could be used to fabricate custom implants with enhanced surface structures to either promote or prevent the adhesion of cells to the implant in specific areas. Similarly, controlled microstructures may be used in a number of microelectronic packaging applications.

[0003] Selective laser micro-sintering (or micro-selective laser sintering “ μ -SLS” or “micro-SLS”) is an additive manufacturing technology that uses a continuous high power laser to manufacture a three-dimensional component (e.g., a part), under condition of vacuum or reduced shield gas pressure, in a layer-by-layer fashion from a powder (e.g., plastic, metal, polymer, ceramic, composite materials, etc.). That is, metal powders are spread onto a powder bed and a continuous laser beam is scanned across the powder bed to sinter together the metal powders at the scanned locations; a new layer of powder is then spread onto the bed over the sintered layer and the process is repeated to build a three-dimensional part.

[0004] There are many challenges to understanding the physics of the process at nanoscale as well as with conducting experiments at that scale; hence, modeling and computational simulations are vital to understand the sintering process physics. At the sub-micron (μ m) level, the interaction between nanoparticles under high power laser heating raises additional near-field thermal issues such as thermal diffusivity, effective absorptivity, and extinction coefficients compared to larger scales. Thus, nanoparticle’s distribution behavior and characteristic properties are very important to understanding the thermal analysis of nanoparticles in a μ -SLS process.

[0005] Therefore, what are needed are devices, systems and methods that overcome challenges in the present art, some of which are described above.

SUMMARY

[0006] Exemplified microscale selective laser sintering (μ -SLS or micro-SLS) systems and methods facilitate modeling of the nanoparticle powder bed by simulating the interactions between particles during the powder spreading operation. In particular, the exemplified methods and system use multiscale modeling techniques to accurately predict the formation and mechanical/electrical properties of parts produced by selective laser sintering of powder beds. Discrete element modeling is used for nanoscale particle interactions by implementing the different forces dominant at nanoscale. The given size distribution of particles with desired boundary conditions are generated. The particles interact with each other and when they settle down at steady state, they have a specific location. This steady state locations are imported into a finite element solver for the analysis of the near field energy transfer. This heat transfer analysis is used to predict the sintering of individual particles in the powder beds in order to build up a complete structural model of the parts that are being produced by the SLS process. By analyzing the near field energy transfer and sintering for the nanoparticles which can be generated by a given size distribution and force interaction, mechanical/electrical properties of parts produced by selective laser sintering of powder beds can be accurately predicted. In addition, the cross section and a detailed particle surface analysis such as temperature distribution are obtained.

[0007] The exemplified methods and systems facilitate the build-up of a complete model of fabricated part including void formation from a set of use specified input parameters. This method is unique in that it builds up a model of the part by analyzing the individual particles that are being sintered and building them up into a complete model of the entire part. This is the first technique that provides the analysis of nanoparticle beds as a whole distribution under the dominant nanoscale force interactions. The exemplified methods and systems takes into account the entire sintering process for the particle level to the part level to create a complete powder-to-part analysis.

[0008] In some embodiments, a general modeling approach is used to better understand the formation of parts in the μ -SLS system. This particle bed is then imported into a multi-physics finite element software package where interactions between the incident laser and the nanoparticle bed are simulated. These simulations are used to generate a temperature profile within the particle bed as a function of time. This temperature profile is coupled with a phase field model of the nanoparticle morphology in a finite element software in order to model the how the nanoparticles become sintered together during the μ -SLS process. Next, a new nanoparticle layer is added to the model and the process is repeated until an entire part is built up. Using the results of these simulations, a 3D model of the fabricated part can be assembled and predictions of the electrical/mechanical properties of the part can be made. The predictions can then be evaluated against the measured properties of the parts produced using the μ -SLS testbed. The μ -SLS testbed is used to validate each step of the simulation and modeling effort.

[0009] In some embodiments, the exemplified methods and systems are used to predict the nanoparticle’s locations at steady state to be used for thermal simulation.

[0010] In some embodiments, the exemplified methods and systems are used to account for and predicts agglomeration in nanoparticle systems.

[0011] In some embodiments, the exemplified methods and systems includes nanoscale heat transfer analysis in modeling the thermal properties of the powder bed with nanoparticles.

[0012] In some embodiments, the exemplified methods and systems are used for optimization of the critical parameters for submicron features.

[0013] In some embodiments, the exemplified methods and systems are used for robust analysis providing flexible parameter adjustment.

[0014] In some embodiments, the exemplified methods and systems are used to create complete part models based just on the size distribution of particles in the powder bed, the geometry of the part and processing parameters such as laser scan speed, laser power, layer thickness and material being sintered.

[0015] According to an aspect, a method is disclosed for fabricating a three-dimensional workpiece, on a layer-by-layer basis, by forming, for each layer, a uniform layer of nanoparticle powders to be selectively sintered. The method includes dispensing a generally uniform layer of nanoparticle ink or a colloid comprising a solvent having a plurality of nanoparticles mixed or suspended therein, wherein the solvent of the layer of colloid evaporates to produce a generally uniform layer of nanoparticles powder on the working surface of the workpiece.

[0016] In some embodiments, the nanoparticle ink or the colloid comprises a metal particle selected from the group consisting of Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Ba, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and combinations thereof.

[0017] In some embodiments, the nanoparticle ink or the colloid has an average particle size selected from the group consisting of about (e.g., within ± 0.5) 8 nanometers (nm), about 9 nm, about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, about 22 nm, about 23 nm, about 24 nm, about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, about 50 nm, about 51 nm, about 52 nm, about 53 nm, about 54 nm, about 55 nm, about 56 nm, about 57 nm, about 58 nm, about 59 nm, about 60 nm, about 61 nm, about 62 nm, about 63 nm, about 64 nm, about 65 nm, about 66 nm, about 67 nm, about 68 nm, about 69 nm, about 70 nm, about 71 nm, about 72 nm, about 73 nm, about 74 nm, about 75 nm, about 76 nm, about 77 nm, about 78 nm, about 79 nm, about 80 nm, about 81 nm, about 82 nm, about 83 nm, about 84 nm, about 85 nm, about 86 nm, about 87 nm, about 88 nm, about 89 nm, about 90 nm, about 91 nm, about 92 nm, about 93 nm, about 94 nm, about 95 nm, about 96 nm, about 97 nm, about 98 nm, about 99 nm, and about 100 nm.

[0018] In some embodiments, the plurality of particles are substantially spherical in shape.

[0019] According to another aspect, a method is disclosed for predicting mechanical and electrical properties of a three-dimensional part produced by selective laser sintering of powder beds, the method comprising: generating, via

processor, a discrete element model (DEM) comprising a plurality of elements each corresponding to a nanoparticle, the plurality of elements, collectively, having a size distribution, discrete element model incorporating gravitational and van der Waals forces; determining, via the processor, a void fraction value for DEM; and determining, via the processor, using a solver, one or more parameters that results in a minimum value for the void fraction.

[0020] In some embodiments, the method includes, importing, the discrete element model, at steady state configuration, into a finite element solver, wherein the finite element solver is configured to solve a near-field energy transfer.

[0021] In some embodiments, the discrete element model facilitates analysis of nanoparticle beds as a whole distribution under the dominant nanoscale force interactions.

[0022] In some embodiments, the discrete element model is used in both a particle-level and a part-level analysis to create a complete powder-to-part analysis.

[0023] In some embodiments, the method includes, optimizing critical parameters (e.g., size distribution of particles in the powder bed, part geometry, laser scan speed, laser power, layer thickness, and material being sintered) for selective laser sintering process to achieve micro-scale features.

[0024] In some embodiments, the method includes, optimizing critical parameters (e.g., size distribution of particles in the powder bed, part geometry, laser scan speed, laser power, layer thickness, and material being sintered) for selective laser sintering process to achieve sub-micron-scale features.

[0025] In some embodiments, the method includes predicting, via the processor, locations of the nanoparticle at steady state.

[0026] In some embodiments, the method includes performing, via the processor, thermal simulation using the locations of the nanoparticle at steady state.

[0027] In some embodiments, the DEM model comprises a number of spherical particles, N_m , with diameter, D_m , and density, ρ_{sm} , wherein each of the N particles is defined within a Lagrangian reference at time t by its position, $X^{(i)}(t)$, linear velocity, $V^{(i)}(t)$, angular velocity, $\omega^{(i)}(t)$, diameter, $D^{(i)}$, density $\rho^{(i)}$, and mass $m^{(i)}$; to position, linear velocity and angular velocities of the i^{th} particle change with time according to Newton's laws as:

$$\frac{dX^{(i)}(t)}{dt} = V^{(i)}(t)$$

$$m^{(i)} \frac{dV^{(i)}(t)}{dt} = F_T^{(i)} = m^{(i)}g + F_d^{(i)}(t) + F_c^{(i)}(t)$$

$$I^{(i)} \frac{d\omega^{(i)}(t)}{dt} = T^{(i)}$$

wherein the total drag force, $F_d^{(i)}$, is found by the summation of pressure and viscous forces, and wherein the net contact force, $F_c^{(i)}$, is the force acting on the particle as a result of contact with other particles and the total force on each particle, $F_T^{(i)}$, is found through the summation of all forces acting on the i^{th} particle.

[0028] In some embodiments, for each two particles in contact, a normal and tangential effective spring stiffnesses

between two particles in contact is calculated using the elastic modulus and Poisson's ratio of the nanoparticles as:

$$\delta_{nij} = \frac{4}{3} \frac{E_m E_l \sqrt{r_{ml}}}{E_m(1 - \sigma_l^2) + E_l(1 - \sigma_m^2)} \delta_{nij}^{1/2}$$

$$k_{t,ij} = \frac{16}{3} \frac{G_m G_l \sqrt{r_{ml}}}{G_m(2 - \sigma_l) + G_l(2 - \sigma_m^2)} \delta_{nij}^{1/2}$$

wherein E_m and E_l are the elastic moduli and σ_m and σ_l are the Poisson ratios for the m^{th} and l^{th} nanoparticles.

[0029] In some embodiments, coefficients of normal restitution matrix and the tangential coefficient of restitution are written as $M \times M$ symmetric matrices for M solid-phases.

[0030] In some embodiments, the van der Waals force interaction between two nanoparticles or between particle and a surface are calculated using the inner and outer cutoff values of the particle or the wall as

$$F = \frac{AR}{12r^2} \left(\left(\frac{\text{Asperities}}{\text{Asperities} + R} \right) + \frac{1}{\left(1 + \frac{\text{Asperities}}{r} \right)^2} \right)$$

$$F = 2\pi\phi R \left(\left(\frac{\text{Asperities}}{\text{Asperities} + R} \right) + \frac{1}{\left(1 + \frac{\text{Asperities}}{r_{inner\ cutoff}} \right)^2} \right)$$

wherein A is the Hamaker constant, R is the equivalent radius, r is the separation distance, ϕ is the surface energy, D is the particle diameter, $rP_{inner\ cutoff}$ and $rP_{outer\ cutoff}$ are the inner and outer cutoff van der Waals value between particle-particle interaction, and asperity, h , is the general definition of roughness and impurity on the surface. $rW_{inner\ cutoff}$ and $rW_{outer\ cutoff}$ are the inner and outer cutoff value between particle-wall interaction.

[0031] In some embodiments, the size distribution is modeled as a Gaussian distribution.

[0032] In some embodiments, the size distribution is modeled as a log-normal distribution.

[0033] In some embodiments, the DEM is initially generated by inserting a random-size particle at a random location in a pre-defined volume until no other particles fits in the volume without overlapping another particle.

[0034] In some embodiments, the method includes, performing, via the processor, a Neighbor Search algorithm to determine which particles are touching or overlapping as neighbors, wherein any two particles i and j that are located at $X^{(i)}$ $X^{(j)}$, and have radii R_i and R_j , are considered neighbors if they satisfy the following condition:

$$|X^{(i)} - X^{(j)}| < K(R_i + R_j)$$

wherein K is an interaction distance constant.

[0035] In some embodiments, the void fraction value is calculated as

$$\text{Fraction} = \frac{\text{Empty}}{\text{Fill}},$$

wherein

$$\text{Empty} = V_{cube} - \sum_{j=1}^n \frac{4}{3} \pi r_j^3,$$

and wherein

$$V_{cube} = \left(\left(\max \left(\text{Position } x + \frac{\text{Diameter}}{2} \right) - \min \left(\text{Position } x - \frac{\text{Diameter}}{2} \right) \right) * \left(\max \left(\text{Position } y + \frac{\text{Diameter}}{2} \right) - \min \left(\text{Position } y - \frac{\text{Diameter}}{2} \right) \right) * \left(\max \left(\text{Position } z + \frac{\text{Diameter}}{2} \right) - \min \left(\text{Position } z - \frac{\text{Diameter}}{2} \right) \right) \right).$$

[0036] In some embodiments, the DEM is used to account for and predict agglomeration in nanoparticle systems.

[0037] In some embodiments, the DEM includes nanoscale heat transfer analysis in modeling the thermal properties of the powder bed with nanoparticles.

BRIEF DESCRIPTION OF THE DRAWINGS

[0038] The components in the drawings are not necessarily to scale relative to each other and like reference numerals designate corresponding parts throughout the several views:

[0039] FIG. 1 depicts a schematic of two particles in contact.

[0040] FIG. 2 depicts a schematic of the Spring-dashpot system.

[0041] FIG. 3 depicts a schematic view of nanoparticles in the domain.

[0042] FIG. 4 depicts a schematic of typical Gaussian distribution.

[0043] FIG. 5 depicts a schematic of typical log-normal distribution.

[0044] FIG. 6 depicts the neighbor search algorithm for "cell-linked list" in 2D scheme.

[0045] FIG. 7 depicts typical agglomeration simulation result showing particle clustering into a single portion of the original $1 \mu m^3$ box.

[0046] FIG. 8 depicts simulations with uniform particle distributions and different van der Waals force.

[0047] FIG. 9 depicts images of nanoparticle agglomeration for 4 different strong van der

[0048] Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0049] FIGS. 10A and 10B depict plots of nanoparticle agglomeration (as void fraction) for 4 different strong van der Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0050] FIG. 11 depicts images of nanoparticle agglomeration for 4 different weak van der Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0051] FIGS. 12A and 12B depict plots of nanoparticle agglomeration (as void fraction) for 4 different weak van der Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0052] FIG. 13 depicts images of nanoparticle agglomeration for 2 different no van der Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0053] FIGS. 14A and 14B depict plots of nanoparticle agglomeration (as void fraction) for 4 different weak van der Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0054] FIGS. 15A and 15B depict images of agglomeration of about 100 nm diameter nanoparticles in powder form and images of about 100-nm diameter nanoparticles spread onto surface and dried.

[0055] FIGS. 16A, 16B, 16C, 16D show a plot of simulated electric field phasor (FIG. 16C) and temperature profile (FIG. 16A) for loosely packed particle bed with uniform particle distribution showing good heat transfer into the bulk of the powder bed (FIG. 16D).

[0056] FIG. 17 shows a part that has been built using this continuum modeling approach. This part was formed by scanning the laser in a square pattern for each build layer.

[0057] FIG. 18 is a diagram of an exemplary micro-selective laser sintering system in accordance with an illustrative embodiment.

[0058] FIGS. 19A and 19B are detailed diagrams of the exemplary micro-selective laser sintering system of FIG. 18 in accordance with an illustrative embodiment.

[0059] FIG. 20 depicts a diagram of a method of operating the μ -SLS system in accordance with an illustrative embodiment.

[0060] FIG. 21 depicts non-exhaustive exemplary three-dimensional parts that may be fabricated with the exemplified micro-SLS systems and the methods.

[0061] FIG. 22 illustrates an exemplary computer that can be used for predicting mechanical and electrical properties of parts produced by selective laser sintering of powder beds.

DETAILED DESCRIPTION

[0062] The nanoparticle powder and nanoparticle ink described herein may be understood more readily by reference to the following detailed description of specific aspects of the disclosed subject matter and the Examples included therein.

[0063] Before the present nanoparticle powder and nanoparticle ink are disclosed and described, it is to be understood that the aspects described below are not limited to specific synthetic methods or specific reagents, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting.

[0064] Also, throughout this specification, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which the disclosed matter pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon.

[0065] General Definitions

[0066] In this specification and in the claims that follow, reference will be made to a number of terms, which shall be defined to have the following meanings.

[0067] Throughout the description and claims of this specification the word “comprise” and other forms of the

word, such as “comprising” and “comprises,” means including but not limited to, and is not intended to exclude, for example, other additives, components, integers, or steps.

[0068] As used in the description and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a composition” includes mixtures of two or more such compositions, reference to “an agent” includes mixtures of two or more such agents, reference to “the component” includes mixtures of two or more such components, and the like.

[0069] “Optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event or circumstance occurs and instances where it does not.

[0070] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. By “about” is meant within 5% of the value, e.g., within 4, 3, 2, or 1% of the value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[0071] It is understood that throughout this specification the identifiers “first” and “second” are used solely to aid in distinguishing the various components and steps of the disclosed subject matter. The identifiers “first” and “second” are not intended to imply any particular order, amount, preference, or importance to the components or steps modified by these terms.

[0072] Nanoparticle Powder and Nanoparticle Ink

[0073] Disclosed herein are nanoparticle powder and nanoparticle ink. As used herein, “nanoparticle” means any structure with one or more nanosized features. A nanosized feature can be any feature with at least one dimension less than 1 μ m in size. For example, a nanosized feature can comprise a nanowire, nanotube, nanoparticle, nanopore, and the like, or combinations thereof. As such, the nanoparticle powder and nanoparticle ink can comprise, for example, a nanowire, nanotube, nanoparticle, nanopore, or a combination thereof.

[0074] In some examples, a plurality of nanoparticles of the nanoparticle powder and nanoparticle ink can comprise a plurality of metal particles. The plurality of metal particles can, for example, comprise a metal selected from the group consisting of Au, Ag, Pt, Pd, Cu, Al, Sn, Pb, Ni, Zn, and combinations thereof. In some embodiments, the plurality of metal particles can comprise a metal selected from the group consisting of Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Ba, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and combinations thereof.

[0075] The plurality of nanoparticles in the nanoparticle powder and nanoparticle ink can have an average particle size. “Average particle size,” “mean particle size,” and “median particle size” are used interchangeably herein, and generally refer to the statistical mean particle size of the particles in a population of particles. For example, the

average particle size for a plurality of particles with a substantially spherical shape can comprise the average diameter of the plurality of particles. For a particle with a substantially spherical shape, the diameter of a particle can refer, for example, to the hydrodynamic diameter. As used herein, the hydrodynamic diameter of a particle can refer to the largest linear distance between two points on the surface of the particle. Mean particle size can be measured using methods known in the art, such as evaluation by scanning electron microscopy, transmission electron microscopy, and/or dynamic light scattering.

[0076] The plurality of nanoparticles in the nanoparticle powder and nanoparticle ink can have, for example, an average particle size of about (e.g., within ± 0.5) 8 nanometers (nm), about 9 nm, about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, about 22 nm, about 23 nm, about 24 nm, about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, about 50 nm, about 51 nm, about 52 nm, about 53 nm, about 54 nm, about 55 nm, about 56 nm, about 57 nm, about 58 nm, about 59 nm, about 60 nm, about 61 nm, about 62 nm, about 63 nm, about 64 nm, about 65 nm, about 66 nm, about 67 nm, about 68 nm, about 69 nm, about 70 nm, about 71 nm, about 72 nm, about 73 nm, about 74 nm, about 75 nm, about 76 nm, about 77 nm, about 78 nm, about 79 nm, about 80 nm, about 81 nm, about 82 nm, about 83 nm, about 84 nm, about 85 nm, about 86 nm, about 87 nm, about 88 nm, about 89 nm, about 90 nm, about 91 nm, about 92 nm, about 93 nm, about 94 nm, about 95 nm, about 96 nm, about 97 nm, about 98 nm, about 99 nm, and about 100 nm.

[0077] In some embodiments, the average particle size can be 8 nanometers (nm) or more (e.g., 9 nm or more, 10 nm or more, 11 nm or more, 12 nm or more, 13 nm or more, 14 nm or more, 15 nm or more, 16 nm or more, 17 nm or more, 18 nm or more, 19 nm or more, 20 nm or more, 21 nm or more, 22 nm or more, 23 nm or more, 24 nm or more, 25 nm or more, 26 nm or more, 27 nm or more, 28 nm or more, 29 nm or more, 30 nm or more, 31 nm or more, 32 nm or more, 33 nm or more, 34 nm or more, 35 nm or more, 36 nm or more, 37 nm or more, 38 nm or more, 39 nm or more, 40 nm or more, 45 nm or more, 50 nm or more, 55 nm or more, 60 nm or more, 65 nm or more, 70 nm or more, or 75 nm or more). In some embodiments, the plurality of nanoparticles of the nanoparticle powder and nanoparticle ink can have an average particle size of 80 nm or less (e.g., 75 nm or less, 70 nm or less, 65 nm or less, 60 nm or less, 55 nm or less, 50 nm or less, 45 nm or less, 40 nm or less, 39 nm or less, 38 nm or less, 37 nm or less, 36 nm or less, 35 nm or less, 34 nm or less, 33 nm or less, 32 nm or less, 31 nm or less, 30 nm or less, 29 nm or less, 28 nm or less, 27 nm or less, 26 nm or less, 25 nm or less, 24 nm or less, 23 nm or less, 22 nm or less, 21 nm or less, 20 nm or less, 19 nm or less, 18 nm or less, 17 nm or less, 16 nm or less, 15 nm or less, 14 nm or less, 13 nm or less, 12 nm or less, 11 nm or less, 10 nm or less, or 9 nm or less). The average particle size of the plurality of nanoparticles of the nanoparticle powder and nanoparticle ink can range from any of the minimum values described above to any of the maximum values described

above. For example, the plurality of nanoparticles of the nanoparticle powder and nanoparticle ink can have an average particle size of from 8 nm to 40 nm (e.g., from 8 nm to 40 nm, from 4 nm to 80 nm, from 8 nm to 20 nm, from 20 nm to 40 nm, from 40 nm to 60 nm, from 60 nm to 80 nm, from 15 nm to 40 nm, or from 25 nm to 35 nm).

[0078] In some examples, the plurality of nanoparticles in the nanoparticle powder and nanoparticle ink can be substantially monodisperse. “Monodisperse” and “homogeneous size distribution,” as used herein, and generally describe a population of particles where all of the particles are the same or nearly the same size. As used herein, a monodisperse distribution refers to particle distributions in which 80% of the distribution (e.g., 85% of the distribution, 90% of the distribution, or 95% of the distribution) lies within 25% of the median particle size (e.g., within 20% of the median particle size, within 15% of the median particle size, within 10% of the median particle size, or within 5% of the median particle size).

[0079] The plurality of nanoparticles in the nanoparticle powder and nanoparticle ink can comprise particles of any shape (e.g., a sphere, a rod, a quadrilateral, an ellipse, a triangle, a polygon, etc.). In some examples, the plurality of nanoparticles of the nanoparticle powder and nanoparticle ink can have an isotropic shape. In some examples, the plurality of nanoparticles of the nanoparticle powder and nanoparticle ink can have an anisotropic shape. In some examples, the plurality of nanoparticles of the nanoparticle powder and nanoparticle ink are substantially spherical.

[0080] Agglomeration and Powder Bed Formation in Microscale Selective Laser Sintering Systems

[0081] Additive manufacturing (AM) has received a great deal of attention for the ability produce three dimensional parts via laser heating. One recently proposed method of making microscale AM parts is through microscale selective laser sintering (μ -SLS) where nanoparticles replace the traditional powders used in standard SLS processes. However, there are many challenges to understanding the physics of the process at nanoscale as well as with conducting experiments at that scale; hence, modeling and computational simulations are vital to understand the sintering process physics. At the sub-micron (μ m) level, the interaction between nanoparticles under high power laser heating raises additional near-field thermal issues such as thermal diffusivity, effective absorptivity, and extinction coefficients compared to larger scales. Thus, nanoparticle’s distribution behavior and characteristic properties are very important to understanding the thermal analysis of nanoparticles in a μ -SLS process.

[0082] Exemplified methods and system presents a discrete element modeling (DEM) of how copper nanoparticles of a given particle size distribution packs together in a μ -SLS powder bed. Initially, nanoparticles are distributed randomly into the bed domain with a random initial velocity vector and set boundary conditions. The particles are then allowed to move in discrete time steps until they reach a final steady state position, which creates the particle packing within the powder bed. The particles are subject to both gravitational and van der Waals forces since van der Waals forces become important at the nanoscale. A set of simulations was performed for different cases under both Gaussian and log-normal particle size distributions with different standard deviations. The results show that the van der Waals interactions between nanoparticles has a great effect on both the

size of the agglomerates and how densely the nanoparticles pack together within the agglomerates. In addition, exemplified methods and systems use a method to overcome the agglomeration effects in μ -SLS powder beds through the use of colloidal nanoparticle solutions that minimize the van der Waals interactions between individual nanoparticles.

[0083] Introduction

[0084] Harnessing heat transfer at the nanoscale is essential for the development of microchips in semiconductors, micro/nanoelectronics, integrated circuits, and micro/nano electromechanical systems. Today, using nanomaterials such as nanowires, carbon nanotubes, graphene, and metal nanoparticles is common in these types of systems. Nanomaterials are generally used in these systems because the thermal, optical, and electromechanical properties of nanomaterials are quite different from the properties of the bulk material and can be tuned by controlling the shape and size of the nanostructure. The key fields where nanomaterials have recently been used in additive manufacturing technologies are microscale selective laser sintering (μ -SLS), three-dimensional (3D) printing, and stereolithography. μ -SLS is a relatively new additive manufacturing technique in which the structures or objects are fabricated from the bottom up by adding materials layer upon layer. In this technique, a laser that has been focused down to approximately 1 μ m is used to sinter together nanoparticles in a designed pattern on each layer before the next layer of nanoparticles is added to the system. This process is then repeated until an entire 3D structure with microscale features is fabricated. Through the use of precise focusing objectives, ultrafast lasers, and nanoparticle based powder beds it is possible to achieve micron scale feature resolutions with this technique.

[0085] μ -SLS has many advantages over other manufacturing techniques in terms of the flexibility, cost, and finishing quality. Furthermore, μ -SLS provides design freedom and has a lower level of waste and harmful chemicals. Using nanoparticles which can be synthesized with different shapes such as rods or spheres for microscale selective laser sintering can also significantly improve the sintering characteristics and the finishing quality of the parts. However, models for nanoparticle interactions and powder bed generation with nanoparticles are not available for SLS at nanoscale. This is because nanoscale modeling offers many challenges; for instance, a continuum model which is used for micro and larger scales is no longer valid. Also, a ray tracing model cannot be used to obtain the extinction and effective absorption coefficient of a powder bed as the laser wavelength is greater than the characteristic length of the particles. Hence, modeling the nanoscale powder bed with nanoparticles for SLS is quite different from modeling micro or larger scales. For example, van der Waals forces, which are the sum of the attractive or repulsive intermolecular attractions between molecules, dominate interactions between the particles at nanoscale. These van der Waals interactions can create significant agglomeration effects in particle beds containing nanoscale powders which are not typically seen in SLS powder beds that contain only microscale powders. These agglomeration effects can significantly reduce the packing density of the particles in the powder bed which can result in significant voids in the final sintered part. Additionally, particle size distribution is another factor affecting the sintering process at the submicron level. Most powder beds with nanoparticles have non-uniform size distributions which effect the sintering

quality and overall shrinking of the parts produced. Hence, it is essential to model the particle-particle interaction at nanoscale accurately in order to understand the overall powder bed and size distribution effect on the selective laser sintering process. Therefore, in order to better understand the parameters that effect void formation in μ -SLS parts, the exemplified methods and systems use discrete element modeling techniques to investigate the role of van der Waals forces and particle size distribution on the packing density of nanoparticles in a μ -SLS powder bed.

[0086] Modeling Approach

[0087] The powder bed, consisting of solid, spherical nanoparticles that are generated by defining a position and radius, is created using the discrete element method (DEM) in a multiphase computational fluid dynamics, MFIX. Particle packings are generated using the MFIX-DEM discrete mass inlet function with each particle interacting with its neighboring particles. The particles are initially distributed randomly within the powder bed domain and are given an initial velocity and an initial set of boundary conditions. Forces such as gravitational and van der Waals forces are also applied to each particle. Material properties such as diameter, density, and different particle size distribution can also be defined by the user. The MFIX-DEM approach is explained in detail in R. Garg, J. Galvin, T. Li, and S. Pannala, 2012, "Documentation of open-source MFIX-DEM software for gas-solids flows," which is incorporated by reference herein in its entirety, and summarized briefly below. The exemplified simulation analysis predicts different force analysis contributions such as van der Waals and gravitational force within given particle distributions.

[0088] 2.1 Discrete Element Method (DEM)

[0089] In the discrete element method (DEM), a number of spherical particles, N_m , with diameter, D_m , and density, ρ_{sm} are used to represent the nanoparticle in the powder bed. The total number of particles in the powder bed is given by the summation of each spherical particle over the total number of solid phases, M , as given by equation (1).

$$N = \sum_{m=1}^M N_m \quad \text{Equation (1)}$$

[0090] Each of the N particles is defined within a Lagrangian reference at time t by its position, $X^{(i)}(t)$, linear velocity, $V^{(i)}(t)$, angular velocity, $\omega^{(i)}(t)$, diameter, $D^{(i)}$, density $\rho^{(i)}$, and mass $m^{(i)}$. The position, linear velocity and angular velocities of the i^{th} particle change with time according to Newton's laws as below:

$$\frac{dX^{(i)}(t)}{dt} = V^{(i)}(t) \quad \text{Equation (2)}$$

$$m(t) \frac{dV^{(i)}(t)}{dt} = F_T(t) = m^{(i)}g + F_d^{(i)}(t) + F_c^{(i)}(t) \quad \text{Equation (3)}$$

$$I^{(i)} \frac{d\omega^{(i)}(t)}{dt} = T^{(i)} \quad \text{Equation (4)}$$

[0091] The total drag force, $F_d(i)$, is found by the summation of pressure and viscous forces. The net contact force, $F_c(i)$, is the force acting on the particle as a result of contact with other particles and the total force on each particle, $F_T^{(i)}$, is found through the summation of all forces acting on the i^{th} particle. Also, the summation of all torques acting on the i^{th} particle is represented by $T^{(i)}$.

[0092] 2.1.1 Contact Forces

[0093] A spring-dashpot model, based on a soft-sphere model of the particles, is used herein for the particle interactions modeling. This model also accounts for the degree of overlapping between two nanoparticles as it imposes no restrictions for multi-particle contacts.

[0094] FIG. 1 depicts a schematic of two particles in contact. For the soft-sphere collision shown in FIG. 1, two particles, i and j, in contact have diameters equal to $D^{(i)}$ and $D^{(j)}$, and are located at positions $X^{(i)}$ and $X^{(j)}$ move with linear velocity, V , and an angular velocity, ω . The normal overlap between the particles is given by equation (5) and the unit vector along the line of contact between each particle is given by equation (6).

$$\delta_n = 0.5(D^{(i)} + D^{(j)}) - |X^{(i)} - X^{(j)}| \quad \text{Equation (5)}$$

$$\eta_{ij} = \frac{(D^{(i)} + D^{(j)})}{|X^{(i)} - X^{(j)}|} \quad \text{Equation (6)}$$

[0095] The relative velocity of the point of contact is given by equation (7) where $L^{(i)}$ and $L^{(j)}$ are the distance to the contact point from the center of each particle.

$$V_{ij} = V^{(i)} - V^{(j)} + (L^{(i)}\omega^{(i)} + L^{(j)}\omega^{(j)}) \times \eta_{ij} \quad \text{Equation (7)}$$

[0096] FIG. 2 depicts a schematic of the Spring-dashpot system. For the soft-sphere model used in this exemplified methods and systems, the overlap between two adjacent particles is represented by a system of springs and dashpots. The springs are used to model elastic interactions between the particles and the dashpots represent the kinetic energy loss due to inelastic collisions. The springs are given stiffness's in both the normal, k_n , and tangential, k_t , directions. These stiffness are dependent on the elastic modulus of the nanoparticles that are interacting. Likewise, the dashpot damping coefficients given to each particle interaction in the normal, η_n , and tangential, η_t , directions is determined by the inelastic scattering losses of each nanoparticle collision. Therefore, the normal and tangential components of the contact force, F_{ij} , at time t, can be decomposed into the spring force, F_{ij}^S , and the dashpot force, F_{ij}^D , as given by equations (8) and (9).

$$F_{ij}(t) = F_{ij}^S(t) + F_{ij}^D(t) \quad \text{Equation (8)}$$

$$F_{ij}(t) = F_{ij}^S(t) + F_{ij}^D(t) \quad \text{Equation (9)}$$

[0097] The normal spring force, F_{ij}^S , at any time during the contact between two nanoparticles can be calculated using Hooke's law with the displacement equal to the overlap, δ_n , between the particles as shown in equation (10).

$$F_{ij}^S = -k_n \delta_n \eta_{ij} \quad \text{Equation (10)}$$

[0098] Similarly, at any time during the contact, the tangential spring force is given by equation (11) where δ_t is the tangential displacement. The tangential displacement at the start of the contact can be calculated as using equation (12).

$$F_{ij}^S = -k_t \delta_t \quad \text{Equation (11)}$$

$$\delta_t = V_{ij} \min\left(\frac{|\delta_n|}{V_{ij} \eta_{ij}}, \Delta t\right) \quad \text{Equation (12)}$$

[0099] 2.1.2 Hertzian Model

[0100] The linear spring-dashpot model described in the previous section only works well for small overlap between nanoparticles. For larger overlaps, the linear model must be replaced by a Hertzian contact model. The Hertzian contact model is described in H.Hertz, "Über die berührung fester elastischer körper" (i.e., "On the Contact of Elastic Solids"), J reine und angewandte Mathematik 1882; 94:156-71.

[0101] In the Hertzian contact model, the normal and tangential effective spring stiffnesses between two particles in contact can be calculated using the elastic modulus and Poisson's ratio of the nanoparticles as shown in equations (13) and (14) where E_m and E_l are the elastic moduli and σ_m and σ_l are the Poisson ratios for the m^{th} and l^{th} nanoparticles. In addition, G_m , and G_l are the shear moduli of each nanoparticle as calculated by equations (15) and (16), and r_{ml} is the effective contact radius as given by equation (17).

$$\delta_{n,ij} = \frac{4}{3} \frac{E_m E_l \sqrt{r_{ml}}}{E_m(1 - \sigma_l^2) + E_l(1 - \sigma_m^2)} \delta_{n,ij}^{1/2} \quad \text{Equation (13)}$$

$$k_{t,ij} = \frac{16}{3} \frac{G_m G_l \sqrt{r_{ml}}}{G_m(2 - \sigma_l) + G_l(2 - \sigma_m)} \delta_{n,ij}^{1/2} \quad \text{Equation (14)}$$

$$G_m = \frac{E_m}{2(1 + \sigma_m)} \quad \text{Equation (15)}$$

$$G_l = \frac{E_l}{2(1 + \sigma_l)} \quad \text{Equation (16)}$$

$$\frac{1}{r_{ml}} = \frac{1}{r^{(m)}} + \frac{1}{r^{(l)}} \quad \text{Equation (17)}$$

[0102] 2.1.3 Relationship between Dashpot Coefficients and Coefficients of Restitution

[0103] The relationship of normal dashpot coefficient η_{nml} and normal coefficient of restitution is given by equation (18) where the effective mass (m_{eff}) and collision time (t_{nml}^{col}) between m^{th} and n^{th} solid-phases are defined as

$$m_{eff} = \left(\frac{m_m m_l}{m_m + m_l} \right) \text{ and } t_{nml}^{col} = \pi \left(\frac{k_{nml}}{m_{eff}} - \frac{n_{nml}^2}{4m_{eff}^2} \right)^{-1/2}.$$

$$\eta_{nml} = \frac{2\sqrt{m_{eff} k_{nml} |\ln e_{nml}|}}{\sqrt{\pi^2 + \ln e_{nml}^2}} \quad \text{Equation (18)}$$

[0104] Time step Δt is taken to be one fiftieth of the minimum collision time (i.e. $\Delta t = \min(t_{col,m}/50)$). The normal spring stiffness coefficient is chosen to be $\sim 10^5$ N/m in order to prevent the time step problems due to the complicated definition of spring coefficients in the simulation. By following the Silbert et al. approach (described in Silbert et al., "Granular flow down an inclined plane: Bagnold scaling and rheology," Phys. Rev. E 64, 051302, 2001, which is incorporated herein in its entirety), the relationship of the tangential spring stiffness coefficient (k_{nml}) and the normal stiffness coefficient (k_n) is defined as

$$k_{nml} = \frac{2}{5} k_{nml}.$$

The tangential damping coefficient and the normal damping coefficient is given as

$$\eta_{nml} = \frac{1}{2} \eta_{nml}.$$

Hence, the coefficient of normal restitution matrix and the tangential coefficient of restitution are written as M×M symmetric matrices for M solid-phases shown in equation (19). As the matrix is symmetric, the top diagonal or lower diagonal values (M(M-1)/2) for normal coefficient of restitution between the particle interactions are set to define the matrix.

$$[e_n] = \begin{bmatrix} e_{n11} & e_{n12} & \dots & e_{n1M} \\ \vdots & \ddots & & \vdots \\ e_{nM1} & e_{nM2} & \dots & e_{nMM} \end{bmatrix} \quad \text{Equation (19)}$$

[0105] 2.1.4 Van Der Waals Forces

[0106] At the nanoscale, van der Waals forces become the dominant force and play an important role on particle interaction. Moreover, the van der Waals force becomes very significant at a very short distance and can cause the agglomeration of nanoparticles. Various van der Waals force models that predict the interactions between two nanospherical particles have been suggested (for example, Li et al. "London-van der Waals adhesiveness of rough particles," Powder Technology 161, 248-255 (2006)). However, the initial van der Waals models did not consider surface roughness, which plays a key role in the adhesion of nanoparticles. In fact, no real surface is smooth at the submicron level; even polished silicon wafers are rough at sub-nanometer scale. Hence, the adhesion of nanoparticles is of significant importance in nanoscale applications such as semiconductor fabrication and drug delivery. Recently more complex models have been used to explain the sphere-sphere van der Waals interaction by including an asperity value which depends on surface roughness. Hence, understanding both the roughness and asperity of the surfaces at nanoscale is crucial for modeling the van der Waals forces accurately and thus for modeling powder bed formation in microscale selective laser sintering.

[0107] The van der Waals force interaction between two nanoparticles or between particle and a surface (i.e., the wall of the simulation box) are calculated using the inner and outer cutoff values of the particle or the wall as given in equation (20) and (21) where A is the Hamaker constant, R is the equivalent radius, r is the separation distance, ϕ is the surface energy, D is the particle diameter, $r_{P_inner\ cutoff}$ and $r_{P_outer\ cutoff}$ are the inner and outer cutoff van der Waals value between particle-particle interaction, and asperity, h, is the general definition of roughness and impurity on the surface. $r_{W_inner\ cutoff}$ and $r_{W_outer\ cutoff}$ are the inner and outer cutoff value between particle-wall interaction.

$$F = \frac{AR}{12r^2} \left(\frac{Asperities}{Asperities + R} + \frac{1}{\left(1 + \frac{Asperities}{r}\right)^2} \right) \quad \text{Equation (20)}$$

$$F = 2\pi\phi R \left(\frac{Asperities}{Asperities + R} + \frac{1}{\left(1 + \frac{Asperities}{r_{inner\ cutoff}}\right)^2} \right) \quad \text{Equation (21)}$$

$$\varphi = \frac{A}{24\pi r_{inner\ cutoff}^2} \quad \text{Equation (22)}$$

[0108] FIG. 3 depicts a schematic view of nanoparticles in the domain. The figure illustrates the followings: r is the particle's distance, h is the asperity or surface roughness, w is the separation distance between wall and the particle, L_w and L_p are the distance parameters used for surface-adhesion cohesion. Typical simulation parameters for each simulation run are given in Table 1.

TABLE 1

Parameter	Value
Minimum Particle Radius	40 nm
Maximum Particle Radius	500 nm
Surface Asperity Size	5 nm
Wall Inner Cutoff Value	1 μ m
Wall Outer Cutoff Value	5 μ m
Particle-to-Particle Spring Constant	10 ⁸ N/m
Particle-to-Wall Spring Constant	10 ⁹ N/m

[0109] 2.1.5 Particle—Particle and Particle—Wall Interaction

[0110] For the nanoparticle-to-nanoparticle interactions, if the inner cutoff radius plus the radii of the two particles is less than the distance parameter, L_p , then the van der Waals interaction is calculated using equation 21. However, if the L_p is greater than this value but less than the outer cutoff radius plus the radii of the two nanoparticles then equation 20 is used to calculate the van der Waals interaction. If the distance between the two particles is greater than outer cutoff distance then the van der Waals interaction between the two particles is assumed to be negligible.

[0111] Similarly, for wall-nanoparticle interactions, if the inner cutoff radius plus the diameter of the nanoparticle is less than L_p then the van der Waals interaction between the particle and the wall is calculated using equation 21. However, if the L_p is greater than this value but less than the outer cutoff radius plus the diameter of the nanoparticle then equation 20 is used to calculate the van der Waals interaction. If the distance between the wall and the particle is greater than outer cutoff distance then the van der Waals interaction between the two particles is assumed to be negligible.

[0112] 2.2 Nanoparticle Size Distribution

[0113] Particle-size distribution within the powder bed can significantly affect the mechanical and thermal characteristics of the powder bed such as the surface plasmon resonances and excitation enhancement which can significantly change the quality of the process and the overall level of part shrinkage. Most nanoparticle powder beds have a non-uniform particle size distribution since it is almost impossible to obtain a uniform, mono-sized nanoparticle powder bed. Particle size distributions have been analyzed to understand the effect different distribution characteristics such as

narrow, broad size and finer, poly-dispersed structures can have on how well particles pack together. The particle size distributions used herein are explained at the following section.

[0114] 2.2.1 Gaussian Distribution

[0115] FIG. 4 depicts a schematic of typical Gaussian distribution. Gaussian distribution is a very useful probability method especially when the number of random variables is very large. The probability density of the Gaussian distribution is given in equation (23) where μ is the mean or median and σ is the standard deviation of the distribution. The variance can also be defined as σ^2 . The Gaussian distribution is non-zero over the region and is symmetric about its median.

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} \left(e^{-\frac{(x-\mu)^2}{2\sigma^2}} \right) \quad \text{Equation (23)}$$

[0116] The distribution is properly normalized as $\int_{-\infty}^{+\infty} P(x)dx=1$. The cumulative distribution, $D(x)$, function can also be defined as in equation (24) where erf is the so-called error function.

$$D(x) = \int_{-\infty}^{+\infty} P(x')dx' = \frac{1}{\sigma\sqrt{2\pi}} \left(e^{-\frac{(x'-\mu)^2}{2\sigma^2}} \right) dx' = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{x-\mu}{\sigma\sqrt{2}} \right) \right] \quad \text{Equation (24)}$$

[0117] 2.2.2 Log-Normal Distribution

[0118] FIG. 5 depicts a schematic of typical log-normal distribution. Log-normal distribution is a continuous distribution whose logarithm has a normal distribution. It is a very common model used in the fields where the boundaries and the threshold of the distribution is estimated or known. Also, it is applied to model continuous random quantities when the distribution is skewed. For example a nanoparticle distribution that has a hard minimum size cutoff at 0 nm but can have some very large particles could be well modeled using the log-normal distribution. The log-normal distribution is given in equation (26) where $x \in (0, \infty)$. Also, μ and σ are called the location and the scale parameter, respectively. These parameters can be related with the mean (μ), standard deviation (σ), and variance (v) of the non-logarithmic values given as in equation (25). Also, mean and the median of the distribution can be defined as exp

$$\left(\mu + \frac{\sigma^2}{2} \right)$$

and $\exp(\mu)$, respectively.

$$\mu = \ln \left(\frac{m}{\sqrt{1 + \frac{v}{m^2}}} \right), \sigma = \sqrt{\ln \left(1 + \frac{v}{m^2} \right)} \quad \text{Equation (25)}$$

-continued

$$P(x) = \frac{1}{\sqrt{2\pi} \sigma x} \exp \left(-\frac{[\ln(x) - \mu]^2}{2\sigma^2} \right) \quad \text{Equation (26)}$$

[0119] The cumulative distribution, $D(x)$, function can also be defined as in equation (27) where erf is the error function.

$$D(x) = \int_{-\infty}^{+\infty} P(x')dx' = \frac{1}{\sqrt{2\pi} \sigma x'} \exp \left(-\frac{[\ln(x') - \mu]^2}{2\sigma^2} \right) dx' = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{\ln(x) - \mu}{\sqrt{2} \sigma} \right) \right] \quad \text{Equation (27)}$$

[0120] 2.2 Computational Details of Particle Bed Formation

[0121] In the particle bed formation algorithm within the MFIX-DEM framework, a nanoparticle with a random size, linear velocity, and angular velocity is initially placed at a random position within a $1 \mu\text{m}^3$ box. Another nanoparticle is then placed within the box at a random position with the constraint that the particles do not initially overlap. This process continues until no additional particles can be placed within the box without overlapping with the particles already in the box. This results in a $1 \mu\text{m}^3$, 3-D box that is full of nanoparticles each with a randomly assigned size, position and initial linear and angular velocities. The $1 \mu\text{m}^3$ box is also organized such that the only particle-wall interactions that occur happen at the bottom of the box. In other words, there is no interaction between the particle-wall at the sides and the top surfaces of the box. The size of the particles in the box is determined by randomly selecting the size of each particle using a particle size distribution function. Three different distribution functions were used herein: (1) a uniform distribution, (2) a Gaussian distribution, and (3) a log-normal distribution.

[0122] Once the initial particle sizes, positions, velocities and boundary conditions are set, a time step is given to the system and the particles are allowed to move and interact. After the time step, the new position of each particle can be calculated and the interactions between particles can be determined from the overlap between particles. These overlap values determine the forces on each nanoparticle and the amount of energy dissipated by each particle in the time step period. A new set of particle positions, velocities, and boundary conditions can then be determined for the next time step. This process is repeated until the particles reach a steady configuration within the powder bed.

[0123] 2.2.1 Time Integration

[0124] A first-order time integration scheme is used to determine the position and the velocity of each particle at each time step. In this scheme, the translational velocity, particle center position, and the angular velocity at time $t+\Delta t$ are obtained from values at time t using equations (28), (29), and (30) where $F_T^{(i)}$ and $T^{(i)}$ are the total force and torque acting on the particle.

$$V^{(i)}(t + \Delta t) = V^{(i)}(t) + \frac{F_T^{(i)}(t)}{m^{(i)}} \Delta t \quad \text{Equation (28)}$$

-continued

$$X^{(i)}(t + \Delta t) = X^{(i)} + V^{(i)}(t + \Delta t)\Delta t \quad \text{Equation (29)}$$

$$\omega^{(i)}(t + \Delta t) = \omega^{(i)}(t) + \frac{T^{(i)}(t)}{I^{(i)}}\Delta t \quad \text{Equation (30)}$$

[0125] 2.2.2 Neighbor Search Algorithm

[0126] FIG. 6 depicts the neighbor search algorithm for “cell-linked list” in 2D scheme. The neighbor search algorithm is one of the most important and time consuming components of any particle-based simulation. Each particle is marked according to the cell in which the center of the particle is located and a “cell-linked list” search algorithm is used to find the particles neighbors. In this algorithm, the simulation is broken down into smaller boxes and only particles within the same box as the particle being investigated or in neighboring boxes are considered. For example, as shown by the 2-D schematic in FIG. 6, if the particle of interest is the one represented by the filled circle, then the particles belonging to the 9 (27 for the 3-D case) adjacent cells, along with particles belonging to the same cell as the particle of interest, are considered as potential neighbors. Thus, only these particles are further checked against the particle of interest for a neighbor contact. By eliminating most of the particles in the box from the search algorithm, the total simulation time is significantly reduced. In this search algorithm, any two particles i and j that are located at $X^{(i)}$ and $X^{(j)}$, and have radii R_i and R_j , are considered neighbors if they satisfy the following condition in equation (31) where K is an interaction distance constant.

$$|X^{(i)} - X^{(j)}| < K(R_i + R_j) \quad \text{Equation (31)}$$

[0127] This search algorithm can, therefore, be used to determine which particles are touching or overlapping as neighbors. This neighbor search algorithm is run for each time step in order to ensure that the simulation does not miss any possible collision between the particles.

[0128] 2.3 van der Waals Interactions

[0129] Agglomeration of nanoparticles is driven by van der Waals interactions between nanoparticles or between a nanoparticle and a surface. For the agglomeration simulations, three general types of van der Waals interactions are considered: (1) a strong van der Waals interaction case where two dry copper particles interact with each other, (2) a weak van der Waals interaction case where the copper nanoparticles are assumed to be incased in a thin polymer or oxide coating, and (3) a no van der Waals interaction case where the particles are assumed to be in a perfect colloidal solution. The strength of the van der Waals interactions in each case set by adjusting the Hamaker constant of the nanoparticle interaction. In this model, there are assumed to be no van der Waals interactions between the top of box and the nanoparticles since in the top layer of the powder bed is open to the environment. Similarly, there are assumed to be no van der Waals forces between the sides of the box and the nanoparticles since each box is a discrete element within the continuous powder bed so particles may travel through these boundaries on the side walls. However, there is assumed to be a van der Waals interaction between the nanoparticles and the bottom surface of the box since the bottom surface will contain the nanoparticles from the previous sintered layer. The Hamaker constants for each of the van der Waals interaction case [12] are given in Table 2.

TABLE 2

Hamaker Constants for Various Types of van der Waals Interactions		
VDW Interaction Case	Particle to Particle Hamaker Constant	Particle to Bottom Wall Hamaker Constant
Strong van der Waals Interaction	28.4×10^{-20} J	14×10^{-20} J
Weak van der Waals Interaction	10×10^{-20} J	14×10^{-20} J
No van der Waals Interaction	0 J	14×10^{-20} J

[0130] 2.4 Particle Size Distributions

[0131] Herein, three different types of particle size distributions were examined: (1) a uniform distribution where all the particles were 100 nm in diameter, (2) a Gaussian distribution with a mean diameter of 100 nm, and (3) a log-normal distribution with a mean diameter of 100 nm. In addition, the Gaussian and log-normal cases were tested with distribution standard deviations of 5 nm, 15 nm, and 25 nm. Limits of 1 nm and 200 nm on the minimum and maximum particle size respectively were also set for both the Gaussian and log-normal distributions. The total number of the particles generated in the $1 \mu\text{m}^3$ simulation box for both the Gaussian and log-normal distributions ranged from 263 particles of the 25 nm standard deviation case to 455 for the 5 nm standard deviation case.

[0132] 2.5 Void Fraction Analysis

[0133] FIG. 7 depicts typical agglomeration simulation result showing particle clustering into a single portion of the original $1 \mu\text{m}^3$ box.

[0134] Void fraction is defined as the volume of empty space divided by the volume of space filled by nanoparticles in the powder bed. Void fraction is an important parameter in determining how well particles will sinter together in a selective laser sintering process and in determining the quality of the final part produced. Herein, the void fraction was calculated using two different methods. In the first method (referred to herein as method 1), the void fraction is found by considering the highest and lowest particles' positions in the x, y, and z-axis and then creating a box that bounds these particles. These new box bounds are then used to determine the maximum volume that the particles could fill (V_{cube}). This method provides a much better analysis than considering the volume of the whole $1 \mu\text{m}^3$ box since the particles will always settle into some subsection of the original box. Once the volume of the bounding box has been found, the void fraction can be found by calculating the volume of all n number of particles in the box and subtracting that volume from the box volume and dividing by the void fraction as shown in equations (32) through (34).

$$\text{Fraction} = \frac{\text{Empty}}{\text{Fill}} \quad \text{Equation (32)}$$

$$\text{Empty} = V_{\text{cube}} - \sum_{j=1}^n \frac{4}{3}\pi r_j^3 \quad \text{Equation (33)}$$

$$V_{cube} = \left(\left(\max \left(\text{Position } x + \frac{\text{Diameter}}{2} \right) - \min \left(\text{Position } x - \frac{\text{Diameter}}{2} \right) \right) * \left(\max \left(\text{Position } y + \frac{\text{Diameter}}{2} \right) - \min \left(\text{Position } y - \frac{\text{Diameter}}{2} \right) \right) * \left(\max \left(\text{Position } z + \frac{\text{Diameter}}{2} \right) - \min \left(\text{Position } z - \frac{\text{Diameter}}{2} \right) \right) \right) \quad \text{Equation (34)}$$

[0135] The second method (referred to herein as method 2) for calculating the void fraction is very similar to the first except that only the change in the height of the agglomerated cluster in the vertical direction is considered when calculating the bounding box. The extent of the bounding box in the two horizontal directions is set to be the width of the original $1 \mu\text{m}^3$ box. This calculation allows us to take into account the effect that clustering of nanoparticles into discrete agglomerates might have on the overall packing density of the nanoparticles in the powder bed. By comparing the void fraction results from each of the two methods it is possible to separate out voids that are created by the packing of the nanoparticles within an agglomerate and the voids that are formed by the agglomeration process itself.

[0136] 2.6 Test Cases

[0137] The objective herein is to quantify and compare the aggregation kinetics and colloidal stability of nanoparticle powder beds with different types of inter-particle interaction forces. In order to pursue that goal, simulations were performed as listed in Table 3.

TABLE 3

Performed Simulation Data with Particle Size Standard Deviations for Each Case in Nanometers			
Simulation Type	Uniform Distribution	Gaussian Distribution	Log-Normal Distribution
No van der Waals	Std: NA	Std: 25,15,5	Std: 25,15,5
Only Weak van der Waals	Std: NA	Std: 25,15,5	Std: 25,15,5
Only Strong van der Waals	Std: NA	Std: 25,15,5	Std: 25,15,5
Weak van der Waals with gravitational	Std: NA	Std: 25,15,5	Std: 25,15,5
Strong van der Waals with gravitational	Std: NA	Std: 25,15,5	Std: 25,15,5

[0138] Results and Discussion—Uniform Distribution of Particles

[0139] FIG. 8 depicts simulations with uniform particle distributions and different van der Waals force. Overall, herein, the uniform distribution of particles will be used as a basis of comparison for evaluating the effect of particle size distribution on the packing quality of the nanoparticles in the $\mu\text{-SLS}$ powder bed. As can clearly be seen in FIG. 8, van der Waals forces play a significant role in the agglomeration of particles at the nanoscale. When the only forces applied to the nanoparticle system are gravitational forces, then the particles are able to find their lowest energy state and pack into an ordered cell. However, when van der Waals forces are present individual particles adhere together before they can reach their lowest energy state which reduces the

packing order. For example, when only gravitational forces are applied to the system the void fraction is approximately 50%. However, when both van der Waals and gravitational forces are applied to the system then the void fraction climbs to approximately 65% due to the agglomeration effects created by the van der Waals forces. Interestingly, when only van der Waals force are considered in the absence of a gravitational driving force, the void fraction is approximately 60%. This reduction in the void fraction in the absence of the gravitational force may be due to the fact the particles take a much longer time to settle into their final positions if there is no global external driving force pushing them towards their final resting position. Therefore, the particle systems without the gravitational force may be able to find a lower energy configuration and better packing than the systems driven by gravitational forces.

[0140] Strong van der Waals Interaction Force Case

[0141] FIG. 9 depicts images of nanoparticle agglomeration for 4 different strong van der Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0142] The effect of particle size distribution on the packing density for a pure copper nanoparticle system can be examined using the strong van der Waals force interaction cases. In these types of systems, the smallest particles in the system have the largest van der Waals forces on them and, therefore, act as nucleation sites for the formation of agglomerates. In general, the particle distributions with the larger standard deviations pack better (lower void fraction) than the distributions with the smaller standard deviations; however, this is not a strong effect and it can be overwhelmed by random variances do the randomized initial conditions placed on the nanoparticles at the start of the simulation. This general effect can be explained by the fact that with the large particle size standard deviations, there are both more very large and very small nanoparticles that all get packed together. Therefore, the small nanoparticles can generally fill into interstitial spaces between the larger particles in order to increase the overall packing density of the system.

[0143] The exception to this trend is the completely uniform distribution which agglomerates in a different way than the distributions with some non-zero standard deviation. In even distributions with the narrowest standard deviations, there are occasionally small particles that can act like a nucleation site to for agglomeration which results in a heterogeneous type nucleation of the agglomerate. However, in the uniform distribution, there are no small particles to act as a preferential nucleation site. This results in homogeneous nucleation of the agglomerate in the uniform distribution case. As a result of this homogeneous nucleation, the uniform distribution tends to have a better packing density than either the small standard deviation Gaussian or log-normal distribution cases. This indicates that it may be the smallest particles in the powder distribution that most effect agglomeration and not the overall uniformity or size distribution of the nanoparticles. Therefore, one strategy to reduce agglomeration would be to eliminate all of the very small particles from the powder bed. However, in practice it may be impossible to create particle distributions without any small particles that can act as nucleation sites. Overall, the results of these simulations show that it is important to be able to measure and evaluate the size distributions of the nanoparticles in a $\mu\text{-SLS}$ powder bed in order to evaluate the effect these nucleation sites will have on void formation.

[0144] FIGS. 10A and 10B depict plots of nanoparticle agglomeration (as void fraction) for 4 different strong van der Waals cases with particle size standard deviations of 5 nm and 25 nm. In FIG. 10A, the void fractions are calculated based on particle's x,y and z direction, i.e., method 1. In FIG. 10B, the based on particle's y direction only ($x=z=1\ \mu\text{m}$), i.e., method 2. As can be seen in FIGS. 10A and 10B, the void fraction calculated using method 1 is always smaller than or equal to the void fraction calculated using method 2 where the entire width of the initial bounding box is considered in the calculation. This makes sense because the horizontal extent of the nanoparticles will always be smaller than or equal to the original $1\ \mu\text{m}^3$ bounding box. Therefore, the ratio of these two void calculation methods can be used as a proxy for the extent of agglomeration in the nanoparticle system and can be used to separate the effect of packing voids from voids caused by agglomeration.

[0145] Results and Discussion—Weak van der Waals Interaction Case

[0146] FIG. 11 depicts images of nanoparticle agglomeration for 4 different weak van der Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0147] FIGS. 12A and 12B depicts plots of nanoparticle agglomeration (as void fraction) for 4 different weak van der Waals cases with particle size standard deviations of 5 nm and 25 nm. In FIG. 12A, the void fractions are calculated based on particle's x,y and z direction, i.e., method 1. In FIG. 12B, the based on particle's y direction only ($x=z=1\ \mu\text{m}$), i.e., method 2.

[0148] van der Waals interactions between nanoparticles can be reduced by coating the copper nanoparticles with a thin oxide or polymer coating. This reduction in the van der Waals forces means that only the very smallest nanoparticles produce a high enough adhesion force to act as nucleation sites for agglomeration. Therefore, there are fewer nucleation sites in the weak van der Waals case than there were in the strong van der Waals case. Because of these fewer number of nucleation sites, the nanoparticles tend to agglomerate into columnar-like crystals as can be clearly seen for the Gaussian, weak van der Waals force case (2b) with a particle size standard deviation of 5 nm as shown in FIG. 11. This produces a relatively efficient packing of the particles within the agglomerate (similar to the strong van der Waals case) but does increase the overall agglomerate size. Without wishing to be bound to a particular theory, this is because the lower number of nucleation sites in the weak van der Waals case cause the agglomerate to generally form from a single nucleation site in the simulation instead of multiple nucleation sites as is the case with the strong van der Waals case. This result can be seen when the void fraction is calculated using method 2. Overall, when the void fractions are calculated for the weak van der Waals case using method 1 they are not significantly different from the void fractions calculated in the strong van der Waals case. However, when the void fractions are calculated using method 2, the weak van der Waals cases produce void fractions that are about 10% larger than those that were produced in strong van der Waals case. This suggests that just reducing the van der Waals interactions between the nanoparticles alone may not be enough to reduce agglomeration in $\mu\text{-SLS}$ powder beds.

[0149] Results and Discussion—No van der Waals (Gravitational Only) Case

[0150] FIG. 13 depicts images of nanoparticle agglomeration for 2 different no van der Waals cases with particle size standard deviations of 5 nm and 25 nm.

[0151] FIGS. 14A and 14B depict plots of nanoparticle agglomeration (as void fraction) for 4 different weak van der Waals cases with particle size standard deviations of 5 nm and 25 nm. In FIG. 14A, the void fractions are calculated based on particle's x,y and z direction, i.e., method 1. In FIG. 14B, the based on particle's y direction only ($x=z=1\ \mu\text{m}$), i.e., method 2.

[0152] One potential method to reduce agglomeration in $\mu\text{-SLS}$ powder beds is to dispense the powder in a liquid as a colloidal solution and then to coat the solution into a uniform layer. This layer can then be allowed to dry in order to produce the new $\mu\text{-SLS}$ powder bed layer. The advantage of this method is that while the particles are in the colloidal solution, surfactants can be used to effectively eliminate van der Waals interactions between the particles. The simulation results indicate that the presence of van der Waals interactions within the powder bed can cause the void fraction in the particle agglomerates to increase by up to 34% for the low standard deviation, Gaussian case and by up to 40% in the low standard deviation, log-normal distribution case.

[0153] In addition, the elimination of the van der Waals interactions eliminates the large scale formation of agglomeration within the $\mu\text{-SLS}$ powder bed. This can be seen by the fact that when the void density is calculated using each of the two methods presented, both methods produce the exact same results. Therefore, the two bar charts created using each of the two void fraction calculation methods in FIGS. 14A and 14B are identical. This indicates that the particles are spreading out to the edges of the initial bounding box, as can be seen in FIG. 13, so that they can form continuous nanoparticle layers. Therefore, one of the key to producing good, uniform sintering layers in $\mu\text{-SLS}$ powder beds is to eliminate the van der Waals interactions between the nanoparticles in the powder beds.

[0154] Comparison to Experimental Results

[0155] FIGS. 15A and 15B depict images of agglomeration of about 100 nm diameter nanoparticles in powder form and images of about 100-nm diameter nanoparticles spread onto surface and dried.

[0156] To validate the predictions made by the simulations presented in the previous section, several nanoparticle surface spreading experiments were performed. First, 100 nm diameter average size copper nanoparticles from various commercial vendors (US Research Nano and MK Impex) were spread onto glass slides and silicon substrates. As shown in FIG. 15A, these nanoparticles tended to agglomerate into very large, discrete assemblies. These agglomerated particles assemblies can be on the order of 100 μm in diameter and can consist of hundreds of thousands of nanoparticles. These agglomerates contain many more particles than it is possible to simulate using the discrete element method, but the results from the DEM simulations do show very similar agglomeration formation within the smaller simulation volume for both the strong and weak van der Waals cases. In addition, samples passivated with oxide, carbon, and polymer coatings were tested to see how much agglomeration takes place in powder beds generated using these types of passivated particles. The passivation coatings are meant to reduce agglomeration the nanoparticles when

they are in powder form by reducing the van der Waals interactions between the particles. However, even with the passivated coatings, significant agglomeration of the nanoparticles was observed. This observed result matches very well what the discrete element model simulations for the weak van der Waals case predict. This indicates that the simulations that include non-zero van der Waals interactions do a good job predicting nanoparticle agglomeration in the μ -SLS powder bed.

[0157] One method to overcome the agglomeration effects due to van der Waals interactions is to dispense the nanoparticles as part of a colloidal solution and then to dry the solution to form the powder layer. To test this method, a commercially available colloidal solution of copper nanoparticles (Applied Nanotech) was spin coated onto a silicon substrate and was dried on a hotplate. As can be seen in FIG. 15B, this method of spreading the copper nanoparticles produces a much more continuous and uniform nanoparticle layer than the powder spreading method. This result matches well with the predictions made by the no van der Waals force discrete element simulation models. Overall, based on this result, it may be possible to create much more uniform nanoparticle beds for μ -SLS using a solution-based deposition method such as spin coating or slot-die coating than by using more traditional powder spreading methods, such as the use of a counter-rotating roller or a doctor blade to spread a dry powder, which are commonly used in larger scale SLS operations.

[0158] Results and Discussion

[0159] Another process in determining how nanoparticles sinter in the μ -SLS bed is determining how heat is transferred within the bed. In order to determine the mechanisms for heat transfer within the bed, several particle-level simulations of the sintering process were set up with both well-ordered and disordered nanoparticle distributions. FIGS. 16A, 16B, 16C, 16D show a plot of simulated electric field phasor (FIG. 16C) and temperature profile (FIG. 16A) for loosely packed particle bed with uniform particle distribution showing good heat transfer into the bulk of the powder bed (FIG. 16D). Temperature distribution in a disordered powder bed as a laser is scanned over its surface, showing very little heat transfer into the bulk of the powder bed when near-field effects not considered.

[0160] In the ordered NP simulation of the laser heating of the NP powder bed where the effects of convection, conduction, and both far-field and near-field radiation are considered in modeling heat transfer within the NP bed, a temperature drop of only $\sim 100^\circ$ C. was observed over the first 10 layers ($\sim 1 \mu\text{m}$) of the NP bed. A similar simulation of a disordered system that did not consider the effects of near-field radiation found that heat did not penetrate more than two NP layers into the bed. This data strongly suggests that near-field radiation plays a key role in nanoparticle sintering and that if near-field radiation effects are not included in the simulation it is more difficult for heat to penetrate into the NP bed.

[0161] Another step in being able to model the μ -SLS process is being able to model full part formation. This is done by taking the optical, thermal, and sintering properties generated for the powder bed from the particle level simulations and experimental results and importing them into a continuum level simulation of the part fabrication process. Continuum models use volume-averaged bulk material properties to represent the behavior of the powder within

each finite volume of the simulation, thus avoiding the need to resolve every powder particle individually. Without wishing to be bound to particular theory, this is advantageous since powder particles are several orders of magnitude smaller than the part being produced, which makes resolving individual particles computationally infeasible when simulating a full-part build. FIG. 17 shows a part that has been built using this continuum modeling approach. This part was formed by scanning the laser in a square pattern for each build layer. The model shows that a square part is not produced by the square pattern because the longer laser dwell times near the corners of the part over exposes those portions of the part. This is a well-known experimental result. These results support the feasibility of combining particle-level simulations and measurements with continuum models in order to be able to generate accurate part geometry and part property predictions.

[0162] Without wishing to be bound to particular theory, new nanoscale physics present in the μ -SLS process fundamentally change the mechanisms of part formation in μ -SLS as compared with macro-SLS and should be considered in modeling final part shape/quality. In an aspect, sintering is driven by grain boundary and surface diffusion as opposed to particle melting. In another aspect, light penetration into the particle bed is driven by scattering and plasmonic effects as opposed to ray optics. In another aspect, heat transfer within the particle bed is dominated by near-field effects as opposed to simple conduction as assumed in macroscale SLS process modeling. Discrete element modeling, experimental verification, and continuum-level modeling can be used to construct a model of the μ -SLS that incorporates nanoscale effects, while also creating simulations that can model full-part formation fast enough to be viable in the manufacturing environment.

[0163] Exemplary micro-SLS System

[0164] FIG. 18 is a diagram of an exemplary micro-selective laser sintering system 100 in accordance with an illustrative embodiment. As shown in FIG. 18, the μ -SLS system 100 includes (1) a spreader mechanism 102 configured to generate the powder bed, (2) an optical system 104 (also referred to as an optical sintering system) configured to write features into the powder bed, (3) an ultrafast laser system 106 configured to sinter the particles (4) a positioning system 108 configured to move and position a build stage 112 between the optical system 104 and the spreader mechanism 102, and (5) a vacuum and vibration isolation 110 systems configured to reduce outside influences that could damage the part quality.

[0165] Still referring to FIG. 18, the nanopowder spreader mechanism 102, in some embodiments, includes a slot die coating system 102 (shown as "slot die coater 120" and "dispensing pump 122") configured to spread uniform layers of nanoparticle inks over a workpiece 114 (shown as "a silicon wafer 114"). The slot die coating system 102 is configured to dispense, in some embodiments, a uniform layer of nanoparticle ink or a colloid comprising nanoparticles suspended or mixed in a solvent. Upon drying (i.e., evaporation of the solvent), the nanoparticles in the nanoparticle ink or colloid settle to form a uniform layer of nanoparticle powder (shown as "powder bed 124"). The build stage 112, which retains the workpiece 114, includes, in some embodiments, a heated sample holder (shown as "heated chip holder 112") configured to accelerate the drying of the nanoparticle inks or colloid to produce the

powder bed 124. The positioning system 108 includes, in some embodiments, an electromagnetic linear actuator 116 configured to move the silicon wafer workpiece 114 under the slot die coater 120. The positioning system 108 further includes, in some embodiments, air bearings 118 configured to guide the motion and ensure that a smooth uniform coating is produced. The positioning system 108 positions the build stage 112 under the optical system 104 for sintering. In some embodiments, the positioning system 108 moves the build stage 112 under the optical system 104 as the nanoparticle ink is drying. In other embodiments, the positioning system 108 moves the build stage 112 under the optical system 104 after the nanoparticle ink has dried. The positioning system 108 includes, in some embodiments, a flexure-based nanopositioning system configured to precisely move and align (e.g., in less than 100 nm resolution, e.g., 40 nm) the powder bed to the optical system 104 and the slot die coater 120 between each sintering operation. In some embodiments, the optical system 104 is attached to a ball screw and micro-stepper motor assembly configured to move the projection optics up to compensate, after the sintering process, for the increased height of the new layer that has been spread on the powder bed.

[0166] FIGS. 19A and 19B, is a detail diagram of the exemplary micro-selective laser sintering system 100 of FIG. 18 in accordance with an illustrative embodiment. As shown in the FIG. 19A, the build stage 112 is positioned, via the linear actuator 116, to a first position 202 such that the workpiece 114 is positioned proximal to a dispensing head 204 of the slot die coater 120. The build stage 112, in some embodiments, is operatively coupled, via air bearings 240, to one or more guide rails 118. The slot die coater 120 is configured to dispense, via a pump 206, from a tank 208, nanoparticle ink or colloid comprising solvent with nanoparticles mixed or suspended therein.

[0167] The build stage 112, in some embodiments, includes a XY positioner 210 to provide fine positioning of the build stage 112 with respect to the slot die coater 120. In some embodiments, the XY positioner 210 comprises an X-axis flexure member and a Y-axis flexure member, each operatively coupled a voice coil 212. Each X-axis and Y-axis flexure member is configured to elastically bend along a respective direction (i.e., x-direction or y-direction). In other embodiments, commercially-available 2-axis positioners having less than 100 μ m resolution may be used. The build stage 112, in some embodiments, includes a Z-axis nanopositioner 214. In some embodiments, the μ -SLS system 100 includes sensors 216 (shown as 216a, 216b) to provide positioning signals (e.g., feedback signals) to the XY flexure positioner 210 and Z-axis nanopositioner 214. In some embodiments, the sensors 214 are interferometry sensors.

[0168] Referring still to FIG. 19A, the slot-die coater 120, in some embodiments, is operatively coupled to a Z-axis actuator 218 configured to adjust the height displacement of the slot-die coater 120 in the Z-direction. In some embodiments, the Z-axis actuator 218 is configured to adjust the height of the slot-die coater 120 to compensate for each sintered layer added to the workpiece 114.

[0169] Referring now to FIG. 19B, the build stage 112 is positioned, via the linear actuator 116, to a second position 222 such that the workpiece 114 is positioned proximal to an objective lens 224 of the optical system 104. In some embodiments, the first position 202 has a displacement that is greater than 1 foot (e.g., between 0.5 and 1 foot, between

1 and 2 feet, between 2 and 3 feet, between 3 and 4 feet, between 4 and 5 feet, between 5-6 feet, between 6 and 10 feet, and greater than 10 feet) from the second position 222.

[0170] The build stage 112, in some embodiments, includes a heating element 236 (e.g., a thermoelectric device, e.g., peltier; a resistive coil; or the like) to heat a surface 238 of the build stage 112 in operative contact, or proximal to, the workpiece 114. The heating element 236, in some embodiments, is configured to accelerate the drying (or evaporation) of the dispensed nanoparticle ink or solvent of the colloid to produce a uniform layer of nanoparticle powder. A temperature sensor (not shown) mounted to the build stage 112 or the surface 238, in some embodiments, is used to provide feedback control for the heating element 236. In some embodiments, the heat element 236 operates continuously. In addition to accelerating the drying of the dispensed nanoparticle ink or solvent of the colloid, the heat element 236 may elevate the temperature of the workpiece, at an elevated temperature as compared to ambient temperature, which may reduce thermal stress between the workpiece and the layer being sintered during the sintering process.

[0171] Referring still to FIG. 19B, the optical system 104 is configured to direct a plurality of pulse lasers to the dispensed layer of nanoparticles (i.e., the uniform layer of nanoparticle powder formed from the dried nanoparticle ink or the dried colloid of solvent and nanoparticle). The optical system 104 is operatively coupled, in some embodiments, via fiber optics 226, to an ultrafast laser 106. The optical system 104 includes one or more micro-mirror array 228, comprising an array of addressable mirror elements, to selectively direct the beam emitted from the laser 106 to the workpiece 114. In some embodiments, the optical system 104 includes a tube lens 230 to direct the reflected beam from the micro-mirror array 228 to the objective lens 224. In some embodiments, the μ -SLS system 100 includes sensors 232 (shown as 232a, 232b) to provide positioning signals (e.g., feedback signals) to the XY flexure positioner 210 and Z-axis nanopositioner 214 to align the build stage 112 to the optical system 104. The optical system 104, in some embodiments, is coupled to a Z-axis actuator 234 configured to adjust the height displacement of the optical system 104 in the Z-direction. In some embodiments, the Z-axis actuator 234 is configured to adjust the height of the optical system 104 to compensate for each nanoparticle powder layer added to the workpiece 114. In some embodiments, the Z-axis actuator 234 includes a ball screw and micro-stepper motor assembly.

[0172] The μ -SLS system 100 includes one or more controller 220 to coordinate the operation of the slot-die coater, the optical system, and various subcomponents of the micro-SLS system.

[0173] The controller may receive a computer-aid-design (CAD) file or STL file having geometric description of the tangible object to direct generation of the three-dimensional workpiece based on the geometric description of the CAD file or STL file.

[0174] FIG. 20 depicts a diagram of a method 300 of operating the μ -SLS system 100 in accordance with an illustrative embodiment. The method 300 include, iteratively building, on a layer-by-layer basis, the workpiece (e.g., 114) by incrementally applying a uniform layer of nanoparticles via a slot-die coater (e.g., 120) on top of the workpiece and incrementally sintering, on a selective basis,

over a broad area, the applied layer of nanoparticles via an optical and laser system (e.g., 104 and 106).

[0175] Specifically, the method 300, at step 302, includes positioning, via a linear actuator (e.g., 116), a build stage (e.g., 112) at a first position (e.g., 102) such that the workpiece 114 located on the build stage (e.g., 112) is positioned proximal to a dispensing head (e.g., 204) of a slot-die coater (e.g., 120).

[0176] At the first position (e.g., 202), the system 100, at step 304, may align the workpiece (e.g., 114), via an X-Y-Z positioners (e.g., 210, 214), to the head (e.g., 204) of the slot-die coater (e.g., 120).

[0177] The system 100, at step 306, may dispense a uniform layer of nanoparticle ink or colloid comprising a solvent having nanoparticles mixed or suspended therein on top of the workpiece (e.g., 114).

[0178] Conclusions

[0179] Exemplified methods and systems provides a particle-particle interaction model to generate a random packing of nanoparticles and an analysis of the packing fraction of Cu nanoparticles of given particle size distribution by means of MFI-X-DEM simulations was presented. Herein, nanoparticles were injected into the domain from the top boundary and allowed to fall under the influence of gravity and van der Waals forces. Once the particles settle, their positions and properties are can be used as an input for the optical model. The extinction and effective absorption coefficient of a powder bed hence can be calculated. The simulations were done for different cases such as for pure copper nanoparticles, copper nanoparticles with a polymer or oxide coating, and copper nanoparticle in a colloidal coating. The coatings and treatments of the nanoparticles can significantly affect the van der Waals interactions between particles. The effects of various types of particle size distributions (uniform, Gaussian, and log-normal) were also studied for different standard deviations. The particles in the simulation are assumed to not initially overlap and to not initially be deformed due to the adhesion or contact effects. The simulations are run until all particles settle on the surface and find their final resting position. Contact forces are obtained by Newton's laws based on the position, the linear, and the angular velocities of each of the individual particles in the simulation. A spring-dashpot model is used for particle interactions between the nanoparticles and between the nanoparticles and the walls of the simulation. The simulation takes an average time of 3×10^5 seconds on an Intel 8-Core Xeon Processor.

[0180] Overall, these simulations show that van der Waals forces have a significant influence on how nanoparticles agglomerate within the μ -SLS powder bed. Nanoparticles subject to strong van der Waals forces agglomerate very rapidly with multiple nucleation points. This leads to non-optimal packing densities but relatively small agglomerates. Nanoparticles subject to weaker van der Waals forces still form agglomerates but the agglomerated assemblies are generally larger and take longer to form than in the strong van der Waals case due to the lower number of potential agglomeration nucleation sites. When van der Waals interactions between the nanoparticles are eliminated, such as in a colloidal suspension of nanoparticles, the nanoparticles are able to form densely packed, continuous nanoparticle layers as opposed to discrete agglomerated particle assemblies. This result suggest a new potential method for creating nanoparticle layers in μ -SLS additive manufacturing sys-

tems using colloidal solutions. However, more work still needs to be done to determine how well nanoparticles deposited from colloidal solutions can be sintered together and to determine what effect residual surfactants from the colloidal suspension might have on the quality of the final sintered part.

[0181] FIG. 21 depicts non-exhaustive exemplary three-dimensional parts that may be fabricated with the exemplified micro-SLS systems and the methods.

[0182] Example Computing Device

[0183] FIG. 22 illustrates an exemplary computer that can be used for predicting mechanical and electrical properties of parts produced by selective laser sintering of powder beds. In various aspects, the computer of FIG. 22 may comprise all or a portion of the development workspace 100, as described herein. As used herein, "computer" may include a plurality of computers. The computers may include one or more hardware components such as, for example, a processor 201, a random access memory (RAM) module 202, a read-only memory (ROM) module 203, a storage 204, a database 205, one or more input/output (I/O) devices 206, and an interface 207. Alternatively and/or additionally, controller 200 may include one or more software components such as, for example, a computer-readable medium including computer executable instructions for performing a method associated with the exemplary embodiments. It is contemplated that one or more of the hardware components listed above may be implemented using software. For example, storage 204 may include a software partition associated with one or more other hardware components. It is understood that the components listed above are exemplary only and not intended to be limiting.

[0184] Processor 201 may include one or more processors, each configured to execute instructions and process data to perform one or more functions associated with a computer for indexing images. Processor 201 may be communicatively coupled to RAM 202, ROM 203, storage 204, database 205, I/O devices 206, and interface b 207. Processor 201 may be configured to execute sequences of computer program instructions to perform various processes. The computer program instructions may be loaded into RAM 202 for execution by processor 201. As used herein, processor refers to a physical hardware device that executes encoded instructions for performing functions on inputs and creating outputs.

[0185] RAM 202 and ROM 203 may each include one or more devices for storing information associated with operation of processor 201. For example, ROM 203 may include a memory device configured to access and store information associated with controller 200, including information for identifying, initializing, and monitoring the operation of one or more components and subsystems. RAM 202 may include a memory device for storing data associated with one or more operations of processor 201. For example, ROM 203 may load instructions into RAM 202 for execution by processor 201.

[0186] Storage 204 may include any type of mass storage device configured to store information that processor 201 may need to perform processes consistent with the disclosed embodiments. For example, storage 204 may include one or more magnetic and/or optical disk devices, such as hard drives, CD-ROMs, DVD-ROMs, or any other type of mass media device.

[0187] Database **2025** may include one or more software and/or hardware components that cooperate to store, organize, sort, filter, and/or arrange data used by controller **2020** and/or processor **2021**. For example, database **2025** may store hardware and/or software configuration data associated with input-output hardware devices and controllers, as described herein. It is contemplated that database **2025** may store additional and/or different information than that listed above.

[0188] I/O devices **2026** may include one or more components configured to communicate information with a user associated with controller **2020**. For example, I/O devices may include a console with an integrated keyboard and mouse to allow a user to maintain a database of images, update associations, and access digital content. I/O devices **2026** may also include a display including a graphical user interface (GUI) for outputting information on a monitor. I/O devices **2026** may also include peripheral devices such as, for example, a printer for printing information associated with controller **2020**, a user-accessible disk drive (e.g., a USB port, a floppy, CD-ROM, or DVD-ROM drive, etc.) to allow a user to input data stored on a portable media device, a microphone, a speaker system, or any other suitable type of interface device.

[0189] Interface **2027** may include one or more components configured to transmit and receive data via a communication network, such as the Internet, a local area network, a workstation peer-to-peer network, a direct link network, a wireless network, or any other suitable communication platform. For example, interface **2027** may include one or more modulators, demodulators, multiplexers, demultiplexers, network communication devices, wireless devices, antennas, modems, and any other type of device configured to enable data communication via a communication network.

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- What is claimed is:
1. A method of fabricating a three-dimensional workpiece, on a layer-by-layer basis, by forming, for each layer, a uniform layer of nanoparticle powders to be selectively sintered, the method comprising dispensing a generally uniform layer of nanoparticle ink or a colloid comprising a solvent having a plurality of nanoparticles mixed or suspended therein, wherein the solvent of the layer of colloid evaporates to produce a generally uniform layer of nanoparticles powder on the working surface of the workpiece.
 2. The method of claim 1, wherein the nanoparticle ink or the colloid comprises a metal particle selected from the group consisting of Be, Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Ba, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and combinations thereof.
 3. The method of claim 1, wherein the nanoparticle ink or the colloid has an average particle size selected from the group consisting of about 8 nanometers (nm), about 9 nm, about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, about 22 nm, about 23 nm, about 24 nm, about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, about 50 nm, about 51 nm, about 52 nm, about 53 nm, about 54 nm, about 55 nm, about 56 nm, about 57 nm, about 58 nm, about 59 nm, about 60 nm, about 61 nm, about 62 nm, about 63 nm, about 64 nm, about 65 nm, about 66 nm, about 67 nm, about 68 nm, about 69 nm, about 70 nm, about 71 nm, about 72 nm, about 73 nm, about 74 nm, about 75 nm, about 76 nm, about 77 nm, about 78 nm, about 79 nm, about 80 nm, about 81 nm, about 82 nm, about 83 nm, about 84 nm, about 85 nm, about 86 nm, about 87 nm, about 88 nm, about 89 nm, about 90 nm, about 91 nm, about 92 nm, about 93 nm, about 94 nm, about 95 nm, about 96 nm, about 97 nm, about 98 nm, about 99 nm, and about 100 nm.
 4. The method of claim 1, wherein the plurality of nanoparticles are substantially spherical in shape.
 5. A method of predicting mechanical and electrical properties of a three-dimensional part produced by selective laser sintering of powder beds, the method comprising:
 - a. generating, via processor, a discrete element model (DEM) comprising a plurality of elements each corresponding to a nanoparticle, the plurality of elements, collectively, having a size distribution, discrete element model incorporating gravitational and van der Waals forces;
 - b. determining, via the processor, a void fraction value for DEM; and

determining, via the processor, using a solver, one or more parameters that results in a minimum value for the void fraction value, wherein the DEM is used to account for and predict agglomeration in nanoparticle systems.

6. The method of claim 5, comprising:

importing, the discrete element model, at steady state configuration, into a finite element solver, wherein the finite element solver is configured to solve a near-field energy transfer.

7. The method of claim 5, wherein the discrete element model facilitates analysis of nanoparticle beds as a whole distribution under dominant nanoscale force interactions.

8. The method of claim 5, wherein the discrete element model is used in both a particle-level and a part-level analysis to create a complete powder-to-part analysis.

9. The method of claim 5, comprising:

optimizing critical parameters for selective laser sintering process to achieve micro-scale features.

10. The method of claim 5, comprising:

optimizing critical parameters for selective laser sintering process to achieve sub-micron-scale features.

11. The method of claim 5, comprising:

predicting, via the processor, locations of the nanoparticle at steady state.

12. The method of claim 11, comprising:

performing, via the processor, thermal simulation using the locations of the nanoparticle at steady state.

13. The method of claim 5, wherein the DEM model comprises a number of spherical particles, N_m , with diameter, D_m , and density, ρ_{sm} , wherein each of the N particles is defined within a Lagrangian reference at time t by its position, $X^{(i)}(t)$, linear velocity, $V^{(i)}(t)$, angular velocity, $\omega^{(i)}(t)$, diameter, $D^{(i)}$, density $\rho^{(i)}$, and mass $m^{(i)}$; to position, linear velocity and angular velocities of the i^{th} particle change with time according to Newton's laws as:

$$\frac{dX^{(i)}(t)}{dt} = V^{(i)}(t)$$

$$m(i) \frac{dV^{(i)}(t)}{dt} = F_T(i) = m^{(i)}g + F_d^{(i)}(t) + F_c^{(i)}(t)$$

$$I^{(i)} \frac{d\omega^{(i)}(t)}{dt} = T^{(i)}$$

wherein a total drag force, $F_d(i)$, is found by a summation of pressure and viscous forces, and wherein a net contact force, $F_c(i)$, is a force acting on the particle as a result of contact with other particles and a total force on each particle, $F_T^{(i)}$, is found through a summation of all forces acting on an i^{th} particle.

14. The method of claim 5, wherein, for each two particles in contact, a normal and tangential effective spring stiffness between two particles in contact is calculated using the elastic modulus and Poisson's ratio of the nanoparticles as:

$$\delta_{n,ij} = \frac{4}{3} \frac{E_m E_l \sqrt{r_{ml}}}{E_m(1 - \sigma_l^2) + E_l(1 - \sigma_m^2)} \delta_{n,ij}^{1/2}$$

$$k_{t,ij} = \frac{16}{3} \frac{G_m G_l \sqrt{r_{ml}}}{G_m(2 - \sigma_l) + G_l(2 - \sigma_m)} \delta_{n,ij}^{1/2}$$

wherein E_m and E_l are elastic moduli, and σ_m and σ_l are Poisson ratios for m^{th} and l^{th} nanoparticles.

15. The method of claim 5, wherein coefficients of normal restitution matrix and tangential coefficient of restitution are written as $M \times M$ symmetric matrices for M solid-phases.

16. The method of claim 5, wherein van der Waals force interaction between two nanoparticles or between particle and a surface are calculated using the inner and outer cutoff values of the particle or the wall as

$$F = \frac{AR}{12r^2} \left(\left(\frac{\text{Asperities}}{\text{Asperities} + R} \right) + \frac{1}{\left(1 + \frac{\text{Asperities}}{r} \right)^2} \right)$$

$$F = 2\pi\phi R \left(\left(\frac{\text{Asperities}}{\text{Asperities} + R} \right) + \frac{1}{\left(1 + \frac{\text{Asperities}}{r_{\text{inner cutoff}}} \right)^2} \right)$$

wherein A is the Hamaker constant, R is an equivalent radius, r is a separation distance, ϕ is a surface energy, D is a particle diameter, $rP_{\text{inner cutoff}}$ and $rP_{\text{outer cutoff}}$ are the inner and outer cutoff van der Waals values between particle-particle interactions, asperity, h , is a general definition of roughness and impurity on a surface, and $rW_{\text{inner cutoff}}$ and $rW_{\text{outer cutoff}}$ are the inner and outer cutoff value between particle-wall interactions.

17. The method of claim 5, wherein the size distribution is modeled as a Gaussian distribution.

18. The method of claim 5, wherein the size distribution is modeled as a log-normal distribution.

19. The method of claim 5, wherein the DEM is initially generated by inserting a random-size particle at a random location in a pre-defined volume until no other particles fits in the pre-defined volume without overlapping another particle.

20. The method of claim 15, comprising:

performing, via the processor, a Neighbor Search algorithm to determine which particles are touching or overlapping as neighbors, wherein any two particles i and j that are located at $X^{(i)}$ and $X^{(j)}$, and have radii R_i and R_j , are considered neighbors upon satisfying condition:

$$|X^{(i)} - X^{(j)}| < K(R_i + R_j)$$

wherein K is an interaction distance constant.

21. The method of claim 5, wherein the DEM includes nanoscale heat transfer analysis in modeling thermal properties of the powder bed with nanoparticles.

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