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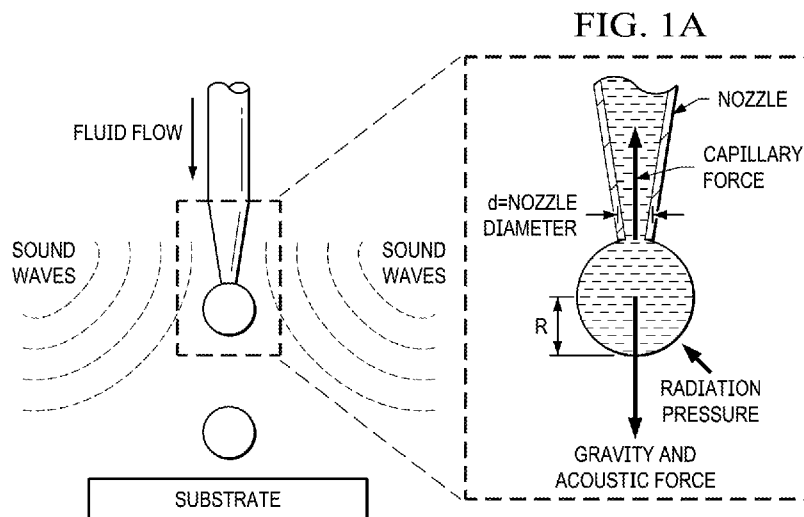
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(57) Abstract: The method comprises arranging a nozzle having a nozzle opening within a first fluid, and generating an acoustic field in the first fluid by an oscillating emitter. A second fluid (an "ink") is driven out of the nozzle, thereby forming a pendant droplet of the second fluid at the nozzle opening. The acoustic field at the nozzle opening is modulated, and acoustic forces from the acoustic field promote detachment of the pendant droplet. Thus, the second fluid or ink is controllably ejected in the first fluid as an ejected droplet. For acoustophoretic printing, the nozzle opening may be positioned in opposition to a printing substrate, and the ejected droplet may be deposited on or in the printing substrate.



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MODULATION OF ACOUSTOPHORETIC FORCES IN ACOUSTOPHORETIC PRINTING

RELATED APPLICATION

[0001] The present patent document claims the benefit of priority under 35 U.S.C. §119(e) to U.S. Provisional Patent Application Serial No. 62/664,467, which was filed on April 30, 2018, and is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0001] The present disclosure relates generally to printing technology and more specifically to acoustophoretic printing.

BACKGROUND

[0002] Due to the limitations of state-of-the-art 2D and 3D printing methods, inks are often engineered to have physical properties satisfying the requirements of existing printers. A typical approach to rendering materials printable is to use additives to adjust the rheological properties of the ink. While enhancing printability, such additives may act as impurities in or otherwise prove detrimental to the printed structure.

[0003] In the realm of droplet-based printing techniques, inkjet technology represents a standard in industry and research. Despite its wide usage, only a narrow window of materials having a suitable combination of properties (*e.g.*, viscosity and surface tension) may be successfully ejected from an ink jet printhead. This limitation can be attributed to the droplet detachment mechanism, which is based on the Rayleigh-Plateau instability. In inkjet technologies, a substantial mechanical excitation of the ink may be required in order to break the meniscus and eject a defined volume of liquid. Such a dynamic process implies a strong coupling between interfacial and viscous forces. From a physical point of view, the droplet generation of a defined ink can be characterized by a non-dimensional number, the Ohnesorge number Oh , and its inverse $Z = Oh^{-1} = (\rho\sigma 2R)^{1/2}/\mu$, with R being the characteristic

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length of the droplet, ρ the density of the liquid, σ its surface tension, and μ its viscosity of the ink. Unsurprisingly, the scientific literature reports that successful printing requires that the physical properties of the ink produce a Z value in a narrow window ($1 < Z < 10$).

[0004] Many inks of practical interest are based upon colloids or polymers that have relatively high viscosity and require dilution with additives for successful printing. Truly decoupling the dependence of the printing process from the physical properties of the ink may allow unprecedented freedom in the type and complexity of materials that can be 2D- and 3D-printed. A description of earlier work to solve this problem may be found in: Foresti *et al.*, "Acoustophoretic Printing Apparatus and Method," U.S. Patents 9,878,536, and 10,214,013; and in Foresti *et al.*, "Apparatus and Method for Acoustophoretic Printing," WO 2018/022513, which are hereby incorporated by reference in their entirety.

SUMMARY

[0005] The method comprises arranging a nozzle having a nozzle opening within a first fluid, and generating an acoustic field in the first fluid by an oscillating emitter. A second fluid (an "ink") is driven out of the nozzle, thereby forming a pendant droplet of the second fluid at the nozzle opening. The acoustic field at the nozzle opening is modulated, and acoustic forces from the acoustic field promote detachment of the pendant droplet. Thus, the second fluid or ink is controllably ejected in the first fluid as an ejected droplet. For acoustophoretic printing, the nozzle opening may be positioned in opposition to a printing substrate, and the ejected droplet may be deposited on or in the printing substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1A is a schematic showing forces on a pendant droplet at a nozzle opening during acoustophoretic printing.

[0007] FIG. 1B shows how droplet volume at detachment varies with acoustic force and nozzle diameter.

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[0008] FIG. 2A is a schematic to illustrate acoustophoretic printing with pulse modulation.

[0009] FIGs. 2B-2H show how droplet volume at detachment varies as a function of printing parameters for pulse modulation.

[0010] FIG. 3A is a schematic to illustrate acoustophoretic printing with a constant acoustic field.

[0011] FIGs. 3B-3E show how droplet volume at detachment varies as a function of printing parameters for a constant acoustic field.

[0012] FIG. 4A is a schematic to illustrate constant mode acoustophoretic printing of a viscoelastic fluid and a typical droplet shape at detachment.

[0013] FIG. 4B is a schematic to illustrate pulsed mode acoustophoretic printing of a viscoelastic fluid and a typical droplet shape at detachment.

[0014] FIG. 5A is an image of an ejected droplet comprising a 4 wt.% Carbopol® solution during constant mode printing.

[0015] FIG. 5B is an image of an ejected droplet comprising a 4 wt.% Carbopol® solution during pulsed mode printing.

[0016] FIG. 5C is an image of an ejected droplet comprising a 3 wt.% alginate solution during constant mode printing.

[0017] FIG. 5D is an image of an ejected droplet comprising a 3 wt.% alginate solution during pulsed mode printing.

[0018] FIGs. 6A-6C illustrate synchronization through pulse modulation.

[0019] FIG. 7 illustrates a typical acoustophoretic nozzle-substrate configuration and ejected droplet trajectories.

[0020] FIG. 8 illustrates typical acoustophoretic droplet deposition with substrate-printhead relative motion, where deposition error can be separated into components orthogonal and parallel to the printing direction.

[0021] FIG. 9 shows the natural oscillation frequency (first mode) of a water droplet according to equation 5.

[0022] FIGs. 10A-10C compare droplet ejection with a constant acoustic force and with amplitude modulation of the acoustophoretic force.

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[0023] FIGs. 11A and 11B show how trajectory error may be reduced with amplitude modulation.

[0024] FIG. 12 illustrates different approaches to controlling the amplitude of the driving frequency to influence the acoustophoretic force.

DETAILED DESCRIPTION

[0025] Described herein is a method to modulate the acoustophoretic field during acoustophoretic printing to allow for unprecedented control over droplet ejection as well as the size, shape, and trajectory of the ejected droplet. The method is applicable to inks having a wide range of Z values, such as from 0.001 to 1000, including both Newtonian and non-Newtonian fluids, viscoelastic fluids, yield stress fluids, polymer solutions, hydrogels, colloids, emulsions and complex fluids in general.

[0026] The method comprises arranging a nozzle having a nozzle opening within a first fluid, and generating an acoustic field in the first fluid by an oscillating or vibrating emitter. The first fluid is capable of transmitting sound waves. A second fluid (the “ink”) is driven out of the nozzle, thereby forming a pendant droplet of the second fluid at the nozzle opening. The acoustic field at the nozzle opening is modulated, and acoustic forces from the acoustic field promote detachment of the pendant droplet. Thus, the second fluid or ink is controllably ejected in the first fluid as an ejected droplet. For acoustophoretic printing, the nozzle opening may be positioned in opposition to a printing substrate, which may comprise a solid, liquid, or a gel, and the ejected droplet may be deposited on or in the printing substrate.

[0027] The modulation may comprise modulating the frequency and/or amplitude of acoustic waves from the oscillating emitter so as to alter the acoustophoretic force on the pendant droplet. Before approaches to modulating the acoustic field are described in detail, the physical principle behind using acoustophoretic force to influence droplet detachment is explained, and various aspects of the acoustophoretic printing method are described.

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[0028] FIG. 1A shows a pendant droplet at the end (nozzle opening) of a nozzle, where gravity acts as an external body force independent of the nozzle/reservoir system. Detachment occurs when the gravitational force $F_g = 4/3\pi R^3 \rho g = V\rho g$, where V is the drop volume and g is gravitational acceleration, exceeds the opposing capillary force $F_c = \pi\sigma d$ for a given nozzle diameter, d , where σ is the surface tension of the drop. Notably, this approach allows for the ejection of droplets of ink having nearly any viscosity, e.g., even droplets of pitch with a viscosity above 10^8 Pa·s. To reduce the droplet volume at detachment, $V = \pi\sigma d/\rho g$, an external force ($\gg 1g$) may be applied to essentially pull on the pendant drop.

[0029] Acoustophoretic forces are independent from any electromagnetic properties and have been used to trap or manipulate droplets within the acoustic field in air. When spherical drops are generated in a standing wave configuration, they are governed by the following force balance:

$$F_c = \pi\sigma d = F_g + F_a = V\rho(g+g_a) \rightarrow V = \pi d\sigma/\rho g_{eq} \quad (1)$$

[0030] where $F_c = \pi\sigma d$, the capillary force, is opposed by both the gravitational force, F_g , and the acoustophoretic force, $F_a \propto R^3 P^2 \propto V P^2$, where R is the drop radius and P is the acoustic pressure. FIGs. 1A and 1B illustrate droplet detachment as described by Equation 1.

[0031] The acoustophoretic droplet ejection process described in Eq. 1 refers to a quasi-static system. It is possible to extend the description to account for the evolution of the droplet size with respect to time using a dynamic model. By feeding the nozzle at a constant flow rate Q , the volume of the pendant drop may evolve as $V(t) = Q \cdot t$, where t represents time. The capillary force F_c , at this level of approximation, is constant, i.e., $F_c = \pi\sigma d = \text{const.}$ Equation 1 becomes:

$$F_g(t) + F_a(t) = V(t)\rho(g+g_a(t)) = Q \cdot t \cdot \rho(g+g_a(t)) \quad (2)$$

[0032] In Equation 2, Q is assumed to be constant and within the dripping regime of the nozzle-liquid. The approach can also be valid in case of $Q(t)$, i.e., where the flow rate is a function of time.

[0033] The acoustic field may be a constant acoustic field, where g_a is a

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constant or the acoustic field may be modulated such that g_a is a function of time.

[0034] In case of constant acoustic field, $g_a = \text{constant}$. Hence, detachment may occur when:

$$V(t)\rho(g+g_a(t)) = Q \cdot t \cdot \rho(g+g_a) = F_c = \pi\sigma d \quad (3)$$

[0035] The droplet may detach at the specific time for which $V(t_d)=V_d$, $V = \pi d\sigma/\rho g_{eq}$.

[0036] When the acoustophoretic acceleration g_a is a function of time (*i.e.*, with a variable acoustic field, $g_a(t)$), the ejection evolution and droplet detachment may be a function of $g_a(t)$. In this case, the droplet detachment may follow the inequality (Eq. 4):

$$Q \cdot t \cdot \rho(g+g_a(t)) \geq F_c = \pi\sigma d \quad (4)$$

[0037] The way $g_a(t)$ is modulated has a key influence on droplet detachment and may fundamentally change the way acoustophoretic droplet ejection works.

[0038] The disclosure now returns to a general description of the method, where the acoustic field is modulated during acoustophoretic printing to control droplet ejection and deposition. As indicated above, a wide range of inks ("second fluids"), including those with a Z value in a range from 0.001 to less than 1, from 1 to 10, or from greater than 10 to 1000, may be successfully printed. The ink or second fluid may comprise, for example, a synthetic or naturally-derived biocompatible material with or without cells (*e.g.*, human cells such as stem cells, primary cells or other cell types), an electrically or ionically conductive material such as a liquid metal (*e.g.*, a gallium-indium eutectic (EGaIn)), and/or a polymer such as an adhesive, a hydrogel, or an elastomer.

[0039] The method may be carried out in an acoustic chamber partially or fully enclosed by sound-reflecting walls, such as described in Foresti *et al.*, "Apparatus and Method for Acoustophoretic Printing," WO 2018/022513, which is hereby incorporated by reference. The acoustic chamber may include the first fluid, *e.g.*, a gas or liquid such as ambient air, water or oil. The acoustic chamber may be immersed in the first fluid.

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In some cases, the first fluid may be forced through the acoustic chamber at a constant or variable flow rate.

[0040] The oscillating emitter may take the form of a piezoelectric transducer, a metal oscillator or another source of sound waves. A suitable driving frequency may be in the range from 1 kHz to 2 MHz, and is more typically from 20 kHz to 250 kHz.

[0041] The nozzle employed for ejection of the second fluid may take the form of a glass pipette, a microfabricated component (e.g., comprising silicon), or another fluid conduit. Typically, the nozzle opening has a diameter in the range from about 1 micron to about 1 mm, and more typically from about 10 microns to about 100 microns. To prevent wetting of the nozzle during printing, the nozzle may include a hydrophobic coating at or near the nozzle opening. Examples of suitable nozzles are described in Foresti, *et al.*, "Nozzle Design for Acoustophoretic Printing," U.S. Provisional Patent Application No. 62/826,436, which is hereby incorporated by reference.

[0042] An advantage of the method is that the size and shape of the ejected droplet may be controlled. Typically, the ejected droplet has a width or diameter less than about 2 mm (or a volume less than about 4 mm³). At higher acoustic fields or with modulation of the acoustic field, as described below, smaller-size droplets may be ejected, such as droplets having a width or diameter less than about 200 microns or a volume less than about 0.004 mm³. In some cases, ejected droplets may have a diameter as small as about 120 microns, or even as small as about 50 microns. A lower bound for the droplet diameter may be about 10 microns. Generally speaking, the ejected droplets have a width or diameter in a range from about 10 microns to about 2 mm, where a width or diameter range of 50 microns to 2 mm, or 200 microns to 2 mm, is more typical. The ejected droplet may have a shape ranging from a teardrop or pear shape to a spherical or ovoid shape, depending on how the acoustic field is modulated.

[0043] As indicated above, modulation of the acoustic field may entail

controlling the frequency and/or amplitude of oscillations from the oscillating emitter.

Pulse Modulation

[0044] In one example, modulation of the acoustic field may entail pulsing the acoustic field in what may be referred to as “pulse mode” or PM modulation. The pulsing may be carried out at a frequency from about 0.01 Hz to about 10,000 kHz, and more typically from 1 Hz to about 1,000 kHz. The pulsing may be on-off pulsing, where the amplitude of a pulse is either 0% or 100% of a peak amplitude. Alternatively, the amplitude of the pulse may vary from 0% to 100% of the peak amplitude. In some cases, the amplitude of the pulse may not return to zero. For example, the amplitude of the pulse may vary from greater than 0% to 100% of the peak amplitude, from 50% to 100% of the peak amplitude, or from 80% to 100% of the peak amplitude. The pulsing may be represented by a waveform selected from a square wave, a triangle wave, a saw tooth wave, or a sinusoidal wave. A duty cycle of the pulsing may range from greater than 0% to less than 100%, and is typically in the range from 10% to 90%, or from 30% to 70%. An ejection velocity of the ejected droplet may increase as the duty cycle of the pulsing increases.

[0045] The detachment frequency of the pendant droplet may be determined by the pulse frequency. The influence of pulse modulation on droplet ejection is illustrated in FIGs. 2A-2H. In this example, $g_a(t)$ is a square wave function with a maximum $g_a = g_{amax} = 5 \text{ g}$ and a duty cycle of 10%. In this case, when $g_{a(t)} = 0$, the minimum droplet size that can be detached is equivalent to simple dripping, *i.e.*, $V_d = V_{drip}$. In the case $g_{a(t)} = g_{amax}$, the minimum possible is $V_{min} = V_{drip} / (g_{amax} + 1)$. Depending on the inequality of Equation (4), the detachment may be determined by the period of pulse modulation, τ_{PM} and its corresponding frequency f_{PM} . With pulse modulation, the ejection frequency f_{eq} of the droplet is constant and determined by the pulsating mode, while the droplet volume at detachment V_d depends on the flow rate Q . Note that g_{amax} and f_{pm} may be chosen to

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take into account Q . In general, to have periodic ejection, $f_{pm}V_d > Q > f_{pm}V_{min}$.

[0046] The impact of pulse modulation on droplet ejection can be appreciated in comparison to droplet ejection without modulation of the acoustic field, that is, for $g_a = \text{constant}$ ("constant mode"), as described above in reference to Equation 3. In this case, for a constant Q and g_a , the ejection is periodic, so $V_d = Q \cdot \tau_{ej}$ with τ_{ej} being the droplet ejection period. By increasing Q , the droplet detachment period may decrease, and its correspondent droplet ejection frequency $f_{ej} = 1/\tau_d$ may increase, as can be seen from FIGs. 3A-3E, and vice versa. Note that in all of these scenarios with varying Q , the droplet volume V_d at detachment stays the same. Only by changing g_a does the droplet size change. Concomitantly, for an equivalent Q , an increased g_a linearly influences f_{ej} , as shown in the figures.

[0047] The main difference between using pulse mode versus constant mode is that with the latter mode the droplet volume at detachment V_d is constant, independent of the flow rate. In contrast, with pulse modulation, the ejection frequency f_{eq} of the droplet is constant and determined by the pulsating mode, while the droplet volume at detachment V_d depends on the flow rate. Both approaches, constant mode (CM) and pulse mode (PM), have advantages, and the choosing between one or another, or a combination of both, may depend on the specific application. For instance, if the priority is monodispersity for a noisy/variable flow rate, then the constant mode may be a good choice. If the priority is keeping ejection frequency constant for a noisy/variable flow rate, the pulse mode may be better suited. It is worth noting that droplet volume scales with the third power of its diameter D . This means that a 15% variation in V_d may still preserve droplet monodispersity (difference in diameter less than 5%). On the other hand, a 15% variation in droplet ejection frequency can be problematic in the case of printing on a substrate, due to loss of resolution/accuracy.

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[0048] Pulsing the acoustic field has many advantages when dealing with high viscosity and viscoelastic fluids (e.g., inks with a Z value from greater than 10 to 1000). Indeed, the presence of a constant field may start to pull the droplet while still attached, elongating the droplet before detachment, resulting in a teardrop/pear shape, or what might be described as a droplet with a tail, as illustrated in FIG. 4A. By using a pulsed acoustic field, this defect can be controlled and/or eliminated, as shown schematically in FIG. 4B. Two prototypical examples of high viscosity/viscoelastic fluids are yield stress fluids, such as a crosslinked polyacrylic acid polymer (e.g., 4 wt.% Carbopol®), or shear thinning fluids, such as a 3 wt.% alginate solution. These inks underwent constant mode and pulsed mode acoustophoretic printing and the shapes of the printed droplets were investigated, as shown in FIGs. 5A and 5B for the 4 wt.% Carbopol® solution and in FIGs. 5C and 5D for the 3 wt.% alginate solution. For Carbopol® solutions, the constant mode experiments were carried out using $d = 100\ \mu\text{m}$, $g_a = 60\text{g}$, and the pulsed mode experiments were carried out using $d = 100\ \mu\text{m}$, $g_a = 60\text{g}$, and $f_{PM} = 0.3\ \text{Hz}$. For alginate solutions, the constant mode experiments were carried out using $d = 90\ \mu\text{m}$, $g_a = 60\text{g}$, and the pulsed mode experiments were carried out using $d = 90\ \mu\text{m}$, $g_a = 60\text{g}$, and $f_{PM} = 3.9\ \text{Hz}$. By comparing the images, it can be observed that the ejected droplet produced in the constant mode experiments (FIG. 5A and FIG. 5C) exhibits a tail that is either diminished (FIG. 5B) or eliminated (FIG. 5D) in the pulsed mode experiments. Consequently, depending on the how the acoustic field is modulated, the ejected droplet may have a non-spherical shape with a tail (e.g., a teardrop or pear shape), or the ejected droplet may exhibit a spherical shape.

[0049] As already mentioned, pulse mode may offer control over the droplet ejection frequency. For specific applications, it might be important to have control over the period of ejection τ_{ej} such that droplet ejection occurs periodically (or aperiodically, if desired). This capability may be used to synchronize droplet ejection for multiple nozzles, as illustrated in

FIGs. 6A-6C. For a plurality of (two or more) nozzles arranged in the first fluid, application of a pulse to each pendant droplet may induce detachment such that droplet ejection is synchronized; in other words, droplet ejection from the multiple nozzles may be controlled so as to occur simultaneously. If the pulses applied to each droplet can be independently controlled, then the synchronization may comprise controlling droplet ejection from the multiple nozzles to occur simultaneously or sequentially, if desired.

[0050] This approach may be particularly beneficial since manufacturing imperfections may present heterogeneity between different nozzles. In addition, parameters such as flow rate Q and/or maximum applied acoustophoretic force g_{amax} may vary with respect to the expected value. As illustrated in FIGs. 6B and 6C, the period of ejection of multiple nozzles may be synchronized even for different values of g_{amax} or for different flow rates Q through the nozzles. Advantageously, using pulsed mode acoustophoretic printing, the pendant droplet may be detached from the nozzle at a predetermined time, ideally with a detachment error of about 200 ms or less. Additionally, for a known ejected droplet velocity and distance from the substrate, the ejected droplet may be deposited onto or into the printing substrate at a predetermined time.

[0051] The synchronization may also be beneficial for improving printing precision. As explained below, a trajectory error ϵ_t and detachment error ϵ_d may be intrinsic to the electrophoretic printing process.

[0052] FIG. 7 shows a typical acoustophoretic nozzle-substrate configuration, and ejected droplet trajectories. The ejection trajectory may have an angle α compared to the vertical trajectory. The accuracy analysis based on $\Delta\alpha$. For the sake of simplicity, $\alpha = 0$ is considered, but the description can be extended to any α .

[0053] In order to calculate and measure the accuracy, there are different approaches. For instance, (1) the variation of the ejection angle α may be measured and/or (2) the droplet placement on the substrate may

be analyzed in a static or dynamic fashion. In the first case, the motion of each droplet may be tracked on two planes (xz and yz) in order to reconstruct droplet deposition on the substrate (FIG. 7, right image). This result can give a specific component of the error, the trajectory error ϵ_t , which is intrinsic to the acoustophoretic printing process. In the second case, droplets may be printed on a substrate. The clear advantage is that it is possible to print a high number of droplets and to simply analyze their position with a single picture. The disadvantage is that for a static target/substrate, there is a limitation to the number of droplets one can print, since they would soon overlap (FIG. 7, right image).

[0054] Thus, an alternative approach is to move the substrate while printing. In such a way, one can recover the error by comparing the droplet position along the ideal trajectory, as illustrated in FIG. 8. Besides its simplicity, this approach also has another advantage: it not only helps to retrieve the trajectory error ϵ_t , but also the detachment error ϵ_d . The detachment error is due to the uncertainty of the timing of droplet ejection. When there is a moving target, this uncertainty may result in an accuracy error. The error can also be classified as orthogonal and parallel errors, defined as orthogonal and parallel to the printing direction. The orthogonal error is due to the trajectory error ϵ_t . The parallel error is due to two components: the trajectory error ϵ_t and detachment error ϵ_d . The trajectory error should, in the assumption of symmetry, be the same in both orthogonal and parallel direction. This means that trajectory error component in the parallel error should be equivalent to the orthogonal error. At this point, the detachment error can be retrieved through the parallel error, by subtracting the orthogonal error.

[0055] The detachment error ϵ_d can be decreased by synchronizing the droplet ejection. As described above, this can be achieved by using pulse modulation to control droplet detachment/ejection. The trajectory error ϵ_t can be decreased by modulating the signal in a different way and time scale using amplitude modulation, as described below.

Amplitude Modulation

[0056] Acoustophoretic forces can be used to induce oscillations on a drop. When the acting force is periodic, it can excite a specific natural oscillation mode n of the drop. This phenomenon has been studied and described by Rayleigh for a small amplitude, inviscid spherical droplet. Within these approximations, the natural frequency of oscillation can be calculated as:

$$\mathbf{[0057] \quad f_n = 1/2\pi \cdot ((\sigma \cdot n(n+1)(n-1)(n+2))/R^3 \Gamma)^{1/2} \quad (5)}$$

[0058] with $\Gamma = \rho_0 n + \rho(n+1)$, and with ρ_0 being the density of the surrounding fluid (in this case, the acoustic medium). FIG. 9 shows the natural frequency of the first resonance mode ($n=2$) for a water droplet in air. The droplet radius was chosen to be within a range of interest for acoustophoretic printing (in particular the zoomed-in plot, right), but it can be generalized for both larger and smaller droplets. Of particular interest is the case of a droplet radius with a resonance frequency comparable with the ultrasonic frequency, for instance, about 25 kHz for $R = 30 \mu\text{m}$ (see circle in FIG. 9, left). It is believed that very interesting phenomenon may arise in this frequency range.

[0059] For acoustophoretic printing, the acoustic force may be modulated by superposing a waveform having a frequency different from an acoustic field frequency to effect amplitude modulation. For example, the acoustophoretic acceleration $g_a(t)$ can be modulated with a frequency f_{AM} that matches the natural frequency of the pendant droplet. Generally speaking, the frequency f_{AM} may be within $\pm 50\%$ a natural frequency of the pendant droplet. FIGs. 10A-10C show both schematic and experimental evidence of this modulation approach. The top images of FIG. 10C were obtained by ejecting water with $d = 80 \mu\text{m}$, $g_a = 60g$ and show droplet behavior under a constant or continuous acoustophoretic force, and the bottom images of FIG. 10C were obtained by ejecting water with $d = 80 \mu\text{m}$, $g_a = 60g$, and $f_{AM} = 270 \text{ Hz}$ and show droplet behavior under an amplitude-modulated acoustophoretic force.

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[0060] Amplitude modulation can be used to reduce lateral oscillations of the pendant droplet and improve the trajectory accuracy of the ejected droplet. In other words, the trajectory error or deviation ϵ_t may be reduced, as illustrated in FIG. 11A for exemplary constant mode and amplitude modulation (AM) mode experiments. The data of FIG. 11B show the standard deviation of droplet deposition position for constant mode and AM mode, where acoustophoretic printing was carried out by ejecting a water-glycerol solution (50 wt.%), $g_a = 87$, $d = 60 \mu\text{m}$, $Q = 296 \text{ nL/s}$, printing speed = 500 mm/min, $f_{AM} = 2.5 \text{ kHz}$. Advantageously, the ejected droplet may be deposited onto or into the printing substrate at a predetermined location with a trajectory error ϵ_t decreased to less than 50% than without amplitude modulation, and an angle trajectory error $\Delta\alpha < 10^\circ$.

[0061] Amplitude modulation can be also used to decrease the droplet size at ejection, since the oscillation induces an additional acceleration to the droplet, resulting in an additional force aiding the detachment. As indicated above, it may be possible to eject droplets having a width or diameter less than about 200 microns or a volume less than about 0.004 mm^3 . In some cases, ejected droplets may have a diameter as small as about 120 microns, or even as small as about 50 microns, where the lower bound for the droplet diameter may be about 10 microns. Generally speaking, the ejected droplets have a width or diameter in a range from about 10 microns to about 2 mm, where the width or diameter is typically in the range from 50 microns to 2 mm, from 200 microns to 2 mm, and/or from 50 microns to 200 microns.

[0062] Amplitude modulation can give a particular shape to a droplet at ejection (by resonating at different natural modes, *i.e.*, $n = 2, 3, 4, \dots$), that can be used to generate a microparticle of a particular shape. For example, the ejected droplet may be cured on the fly while still oscillating to generate the microparticle. Generally speaking, amplitude modulation may permit achieving a pendant droplet with a predetermined shape (*e.g.*, teardrop, sphere, ovoid) at detachment. It is important also to consider the special case when f_{AM} is around the natural oscillation frequency f_n and within the

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same order of magnitude of the main (driving) frequency f or one of its harmonics, e.g., $f = 25$ kHz, with harmonics $2f$, $3f$, ...etc.

[0063] In order to control $g_a(t)$ for acoustophoretic printing, several solutions can be implemented: (1) the amplitude of the driving frequency f may be controlled; (2) the geometry of any resonators may be controlled; (3) the acoustic properties of the medium may be controlled; and/or (4) combinations of these.

[0064] A straightforward way to act on the acoustophoretic force is by changing the amplitude of the sound wave, e.g., controlling the amplitude of the driving frequency (carrier signal). The sound wave can have any shape, as well as its modulation. A practical example is shown in Figure 13. The carrier signal f without any modulation corresponds to constant mode (CM) printing. Using a pulse mode style of modulation of the carrier signal f with any wave form at a frequency f_{pm} results in pulse mode (PM) printing. Amplitude modulation may be obtained by modulating at a different frequency f_{AM} and waveform than the carrier frequency, resulting in amplitude modulation (AM) mode printing. The frequency of the waveform may be lower than the acoustic field frequency, as shown in FIG. 13. Combining all of these approaches together is also possible. In the specific case of improving ejection accuracy, both PM and AM may be used simultaneously.

[0065] Also or alternatively, the main frequency f may be changed, e.g., by using resonators, for instance through a wave guide or a subWAVE (e.g., as described in Foresti *et al.*, U.S. Patent 10,214,013, "Acoustophoretic Printing Apparatus and Foresti *et al.*, WO/2018/022513A1, "Apparatus and Method for Acoustophoretic Printing," which are hereby incorporated by reference in their entirety). In this case, the amplitude of the force depends on the matching between the geometry of the resonators and the exciting frequency(ies). By changing the sound frequency, the resonator may be in resonance or not, directly influencing the amplitude and distribution of the acoustic field within the chamber (e.g., within a chamber outlet or subWAVE) and therefore the

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acoustophoretic force on the droplet. Also or alternatively, the geometry of the resonator(s) may be controlled. Since the resonators may be designed for a specific wavelength, a change in the geometry of the resonators may alter the resonance frequency. Modulation of the acoustic field may also or alternatively be achieved by modifying the oscillating emitter. For example, the dimensions (size) or geometry of the oscillating emitter may be changed.

[0066] Also or alternatively, the acoustic medium ("first fluid"), which may be a gas such as air or a liquid such as water or oil, may be selected to influence $g(t)$. The wavelength of an acoustic wave depends on the medium. By changing the property of the medium (for instance, its density or temperature), the wavelength of the acoustic wave may change as well. This can be used to set the system on/off resonance, influencing the resulting acoustophoretic force. In practice during acoustophoretic printing, modulation of the acoustic field may be achieved by changing the temperature of the first fluid.

[0067] In summary, modulation of the acoustic field to influence acoustophoretic printing may be achieved using any combination of the following: modulating amplitude, frequency, resonator size or geometry, emitter size or geometry, and/or temperature of the first fluid.

[0068] Although the present invention has been described in considerable detail with reference to certain embodiments thereof, other embodiments are possible without departing from the present invention. The spirit and scope of the appended claims should not be limited, therefore, to the description of the preferred embodiments contained herein. All embodiments that come within the meaning of the claims, either literally or by equivalence, are intended to be embraced therein.

[0069] Furthermore, the advantages described above are not necessarily the only advantages of the invention, and it is not necessarily expected that all of the described advantages will be achieved with every embodiment of the invention.

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CLAIMS

1. A method of acoustophoretic printing, the method comprising:
arranging a nozzle within a first fluid, the nozzle having a nozzle opening;
generating an acoustic field in the first fluid by an oscillating emitter;
driving a second fluid out of the nozzle, thereby forming a pendant droplet of the second fluid at the nozzle opening; and
modulating the acoustic field at the nozzle opening,
wherein acoustic forces from the acoustic field promote detachment of the pendant droplet, the second fluid thereby being ejected in the first fluid as an ejected droplet.
2. The method of claim 1, wherein modulating the acoustic field comprises pulsing the acoustic field, and wherein the pendant droplet is detached at a detachment frequency determined by the pulsing.
3. The method of claim 2, wherein a frequency of the pulsing is from 0.01 Hz to 10,000 kHz.
4. The method of claim 2 or 3, wherein the pulsing is carried out with a waveform selected from the group consisting of: square wave, triangle wave, saw tooth wave, sinusoidal wave.
5. The method of any one of claims 2-4, wherein an amplitude of the pulsing varies from greater than 0% to 100% of a peak amplitude.
6. The method of claim 5, wherein the amplitude of the pulsing varies from 50% to 100% of the peak amplitude.
7. The method of any one of claims 2-6, wherein an ejection velocity of the ejected droplet increases as a duty cycle of the pulsing increases.

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8. The method of any one of claims 1-7, wherein the pendant droplet is detached from the nozzle at a predetermined time with a detachment error less than 200 ms.

9. The method of any one of claims 1-8, further comprising a plurality of the nozzles arranged in the first fluid, and wherein the detachment of the pendant droplets from the nozzle openings is synchronized.

10. The method of any one of claims 1-9, wherein the ejected droplet comprises a spherical shape.

11. The method of any one of claims 1-10, wherein the second fluid comprises a Z value in a range from 0.001 to 1000.

12. The method of claim 11, wherein the Z value is from greater than 10 to 1000.

13. The method of any one of claims 1-12, wherein the nozzle opening is positioned in opposition to a printing substrate comprising a solid, liquid, or a gel.

14. The method of 13, wherein the ejected droplet is deposited onto or into the printing substrate at a predetermined location with an angle trajectory error $\Delta\alpha < 10^\circ$.

15. The method of any one of claims 1-14, wherein modulating the acoustic force comprises superposing a waveform having a frequency different from an acoustic field frequency, thereby effecting amplitude modulation of the acoustic force.

16. The method of claim 15, wherein the frequency of the waveform is within +/-50% a natural frequency of the pendant droplet.

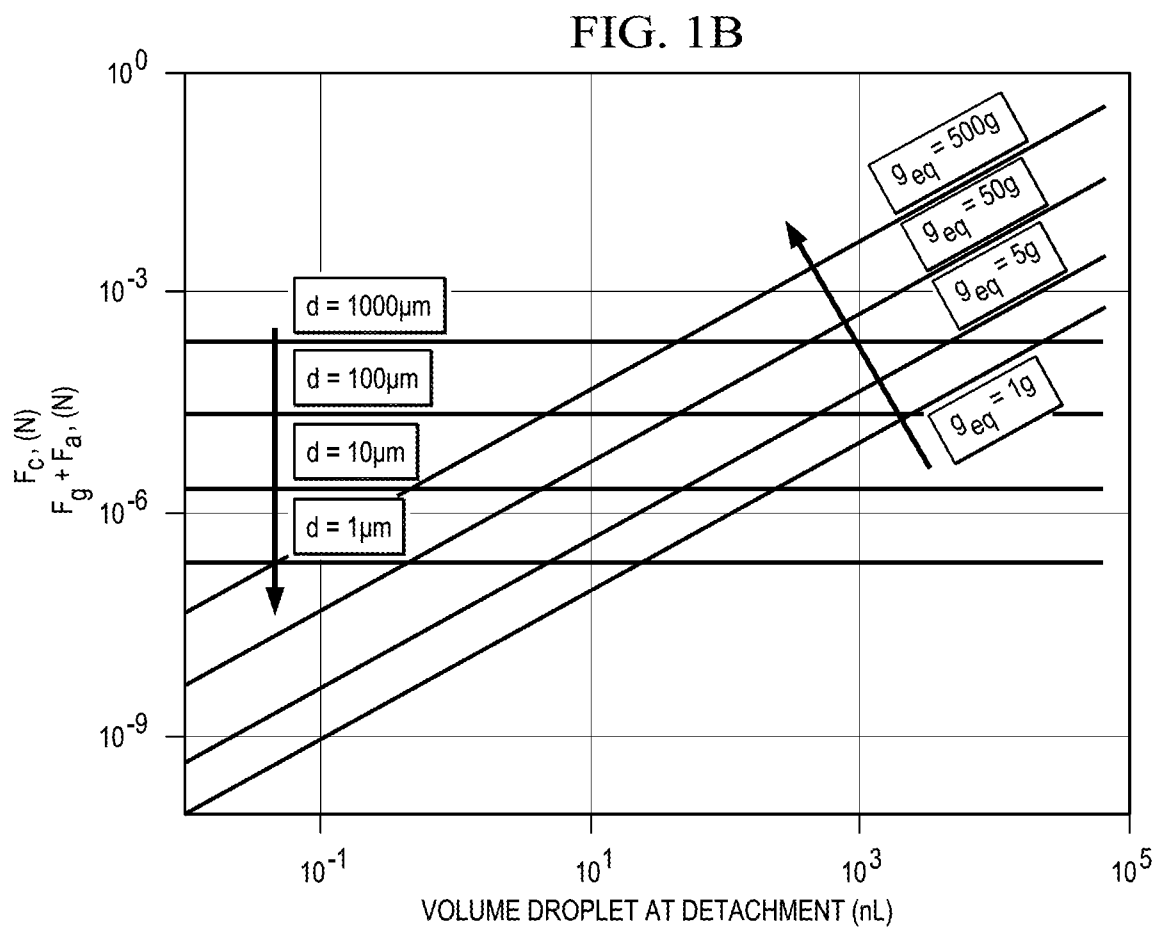
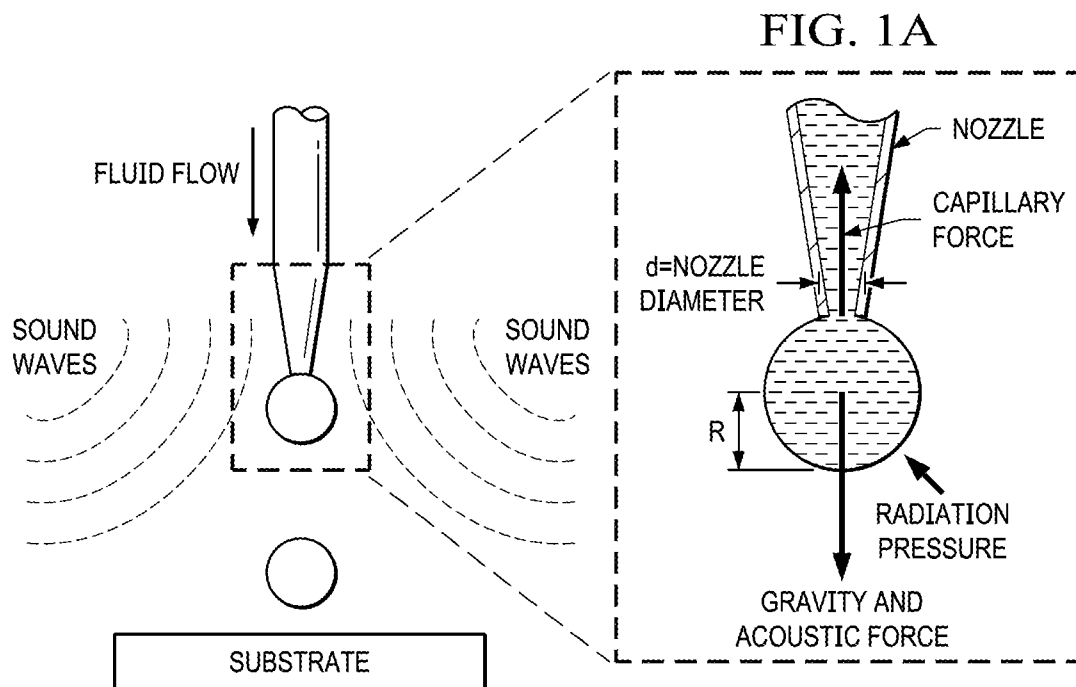
17. The method of claim 15 or 16, wherein the frequency of the waveform is lower than the acoustic field frequency.

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18. The method of any one of claims 15-17, wherein a size of the pendant droplet at detachment is reduced due to the amplitude modulation, a width or diameter of the pendant droplet being less than about 200 microns.

19. The method of any one of claims 1-18, wherein the pendant droplet has a predetermined shape at detachment selected from a sphere, an ovoid and a teardrop.

20. The method of any one of claims 1-19, wherein the modulation of the acoustic field is due to any combination of modulating amplitude, frequency, resonator size or geometry, emitter size or geometry, and/or temperature of the first fluid.



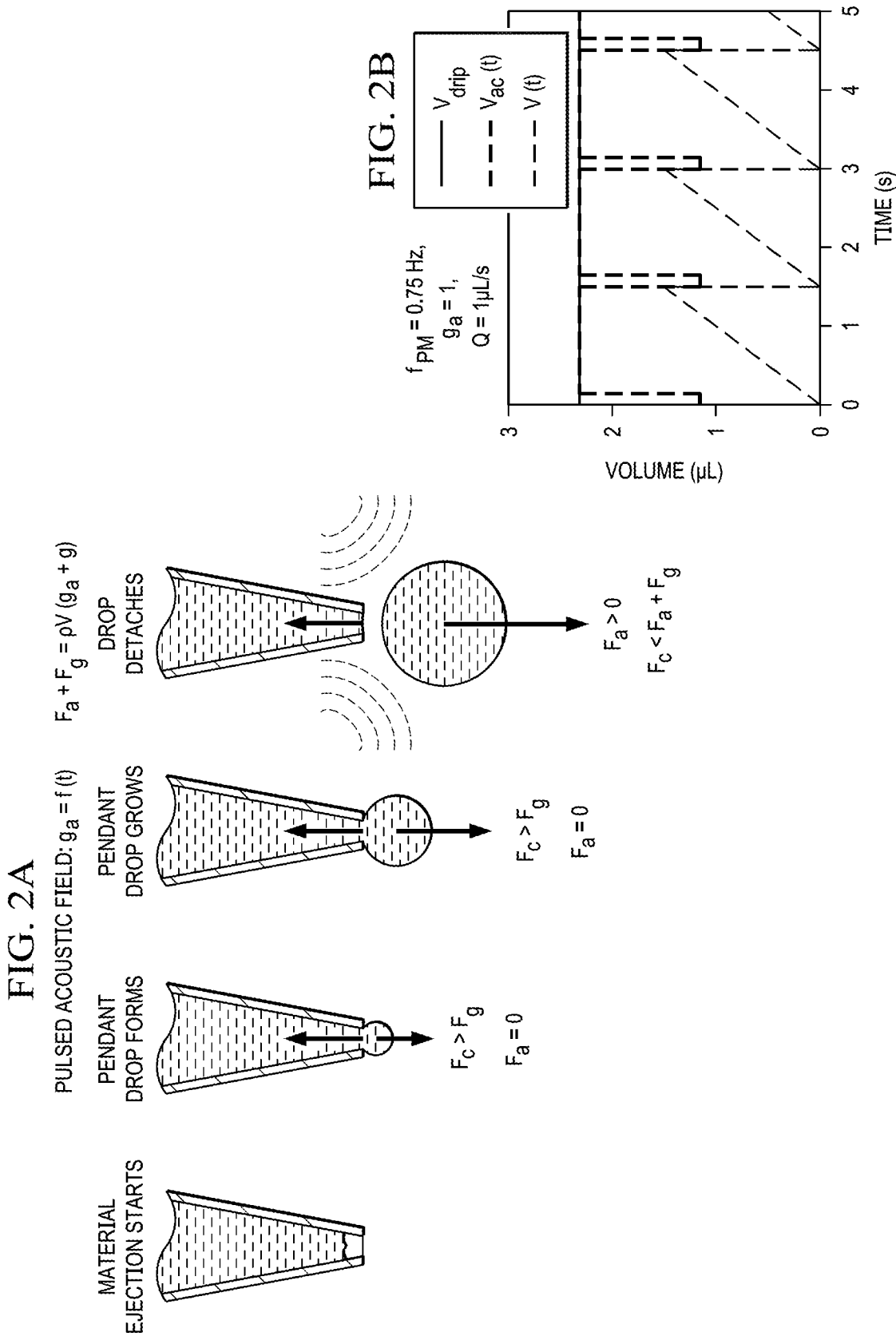


FIG. 2C

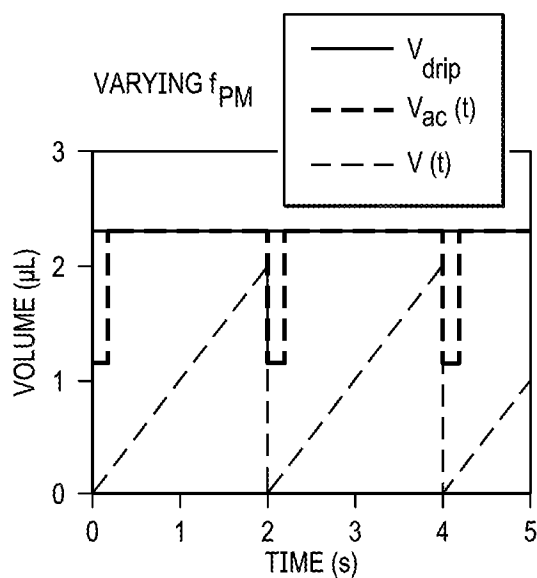


FIG. 2E

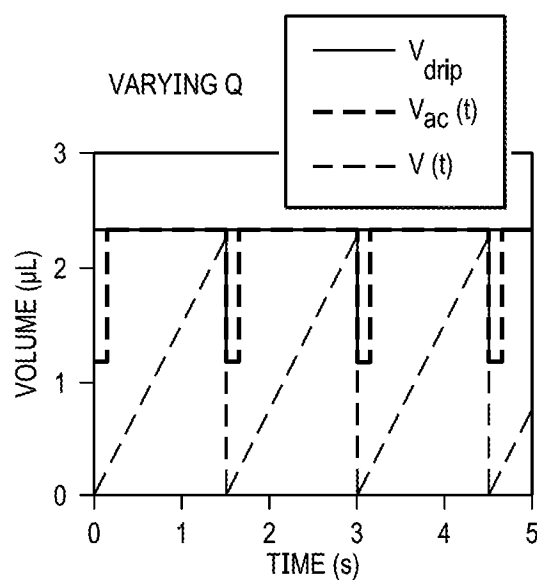


FIG. 2D

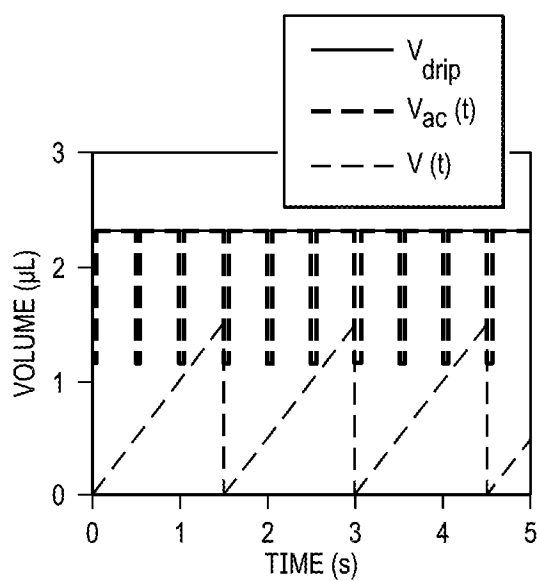
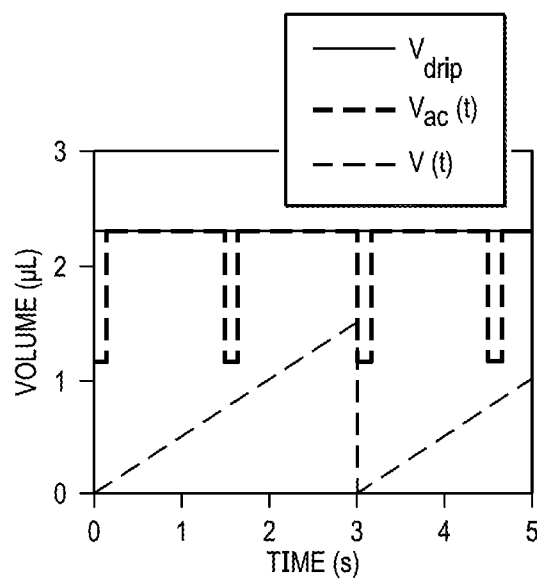


FIG. 2F



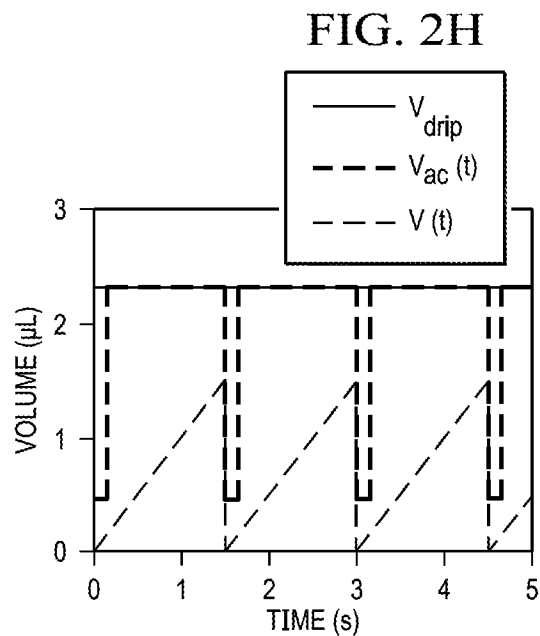
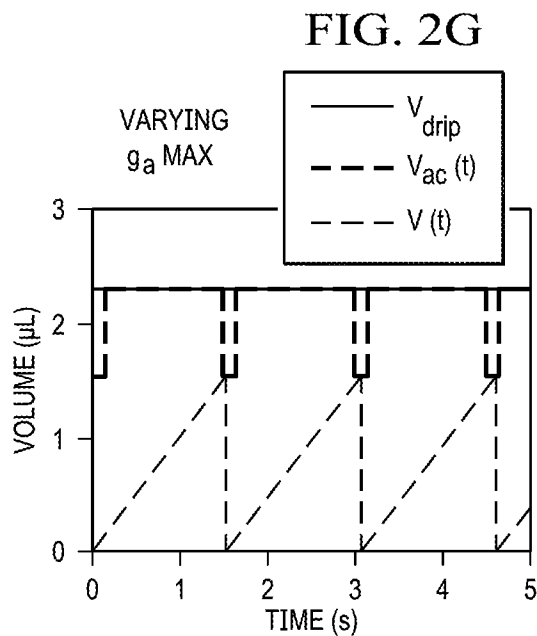
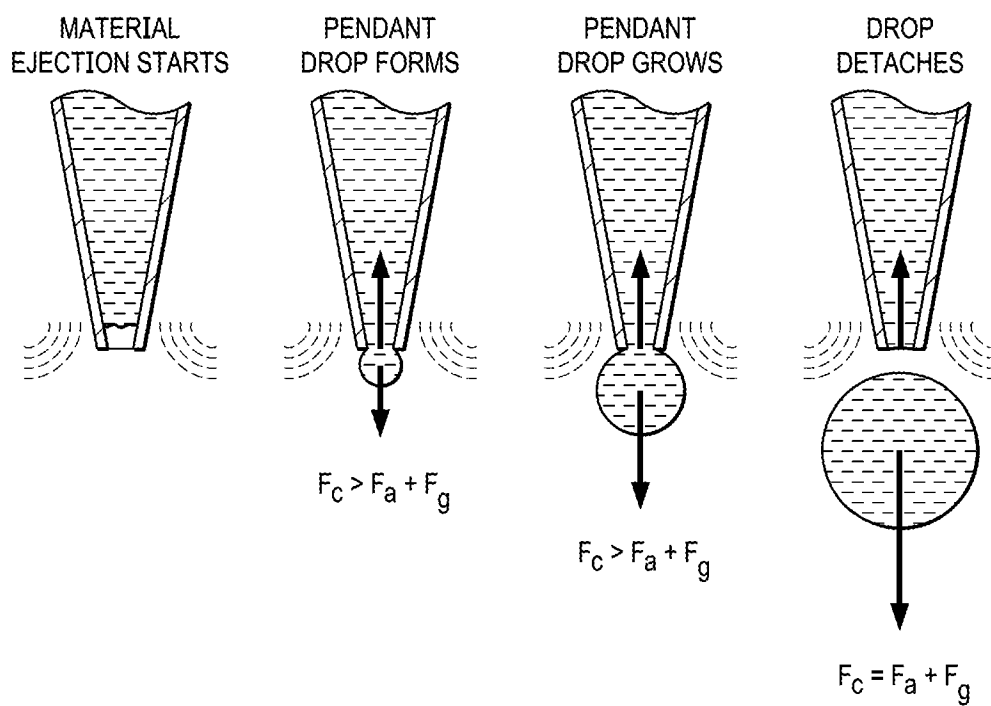
**FIG. 3A**CONSTANT ACOUSTIC FIELD: $g, g_a = \text{CONST}$ 

FIG. 3B

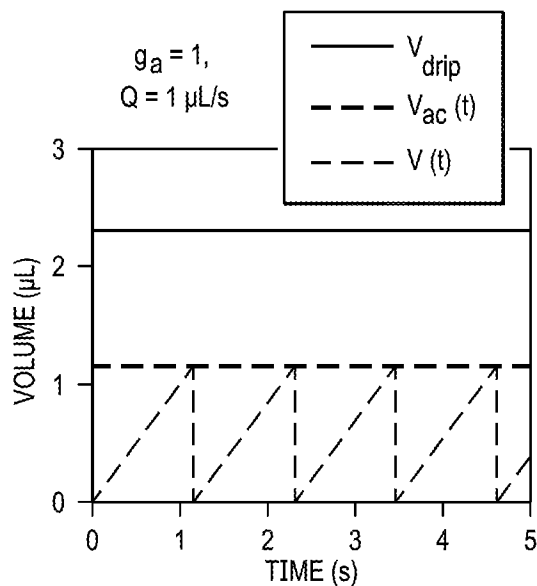


FIG. 3D

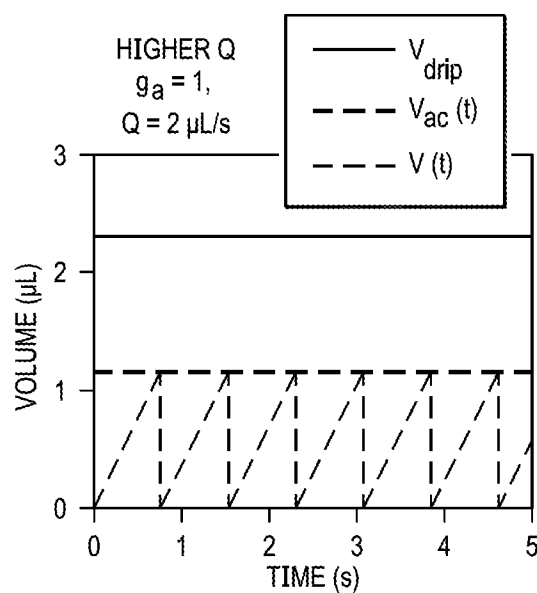


FIG. 3C

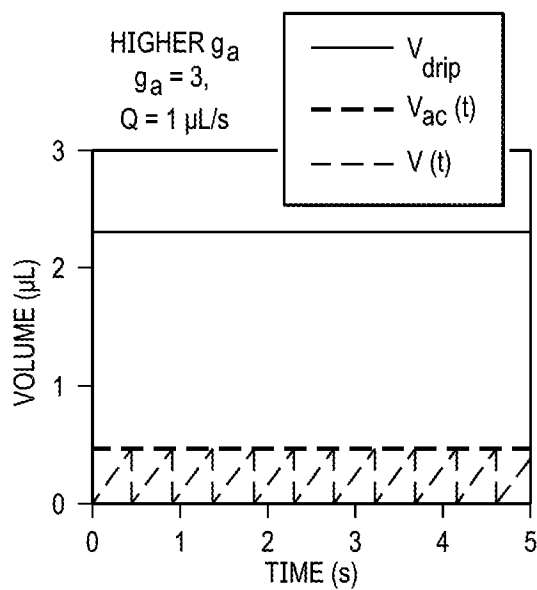


FIG. 3E

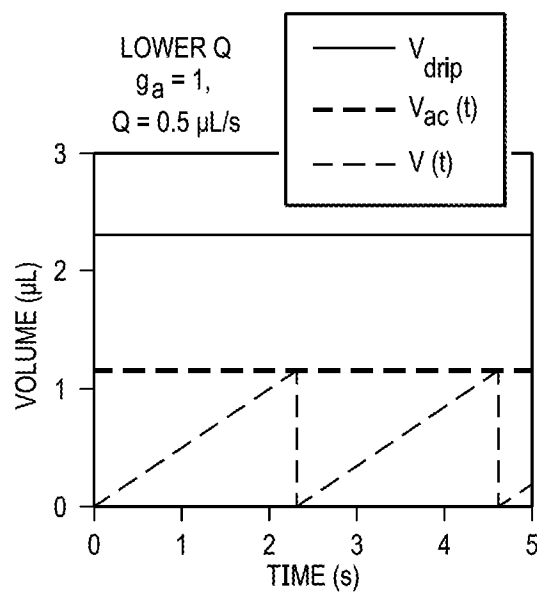


FIG. 4A

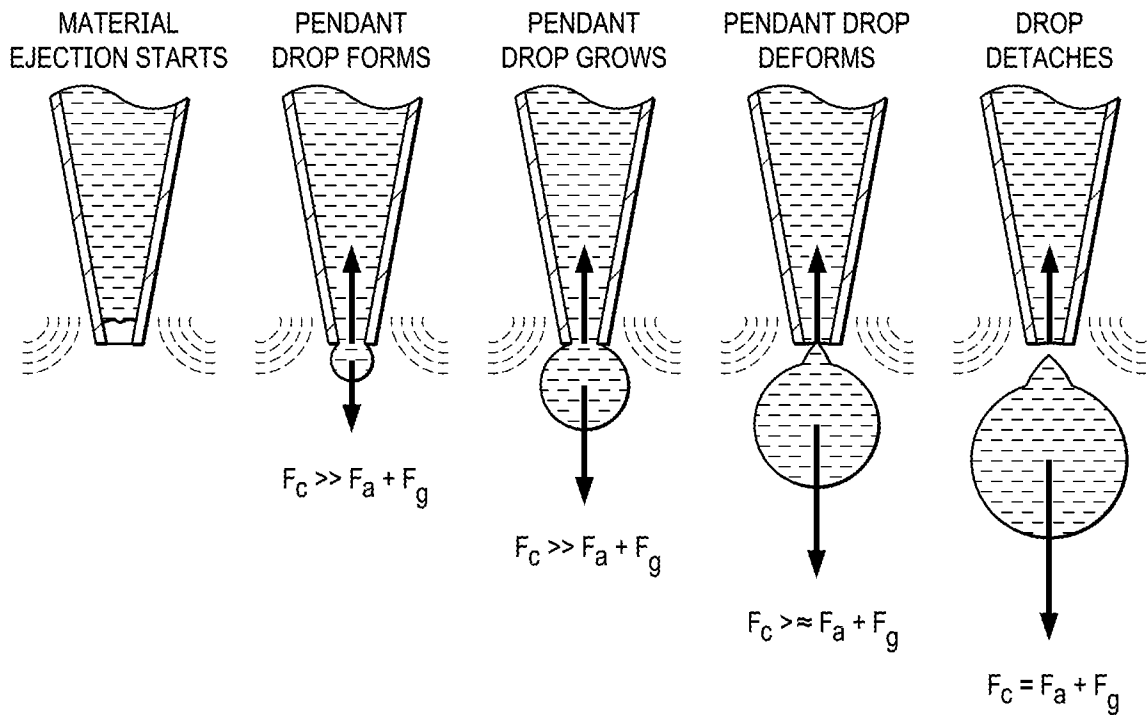
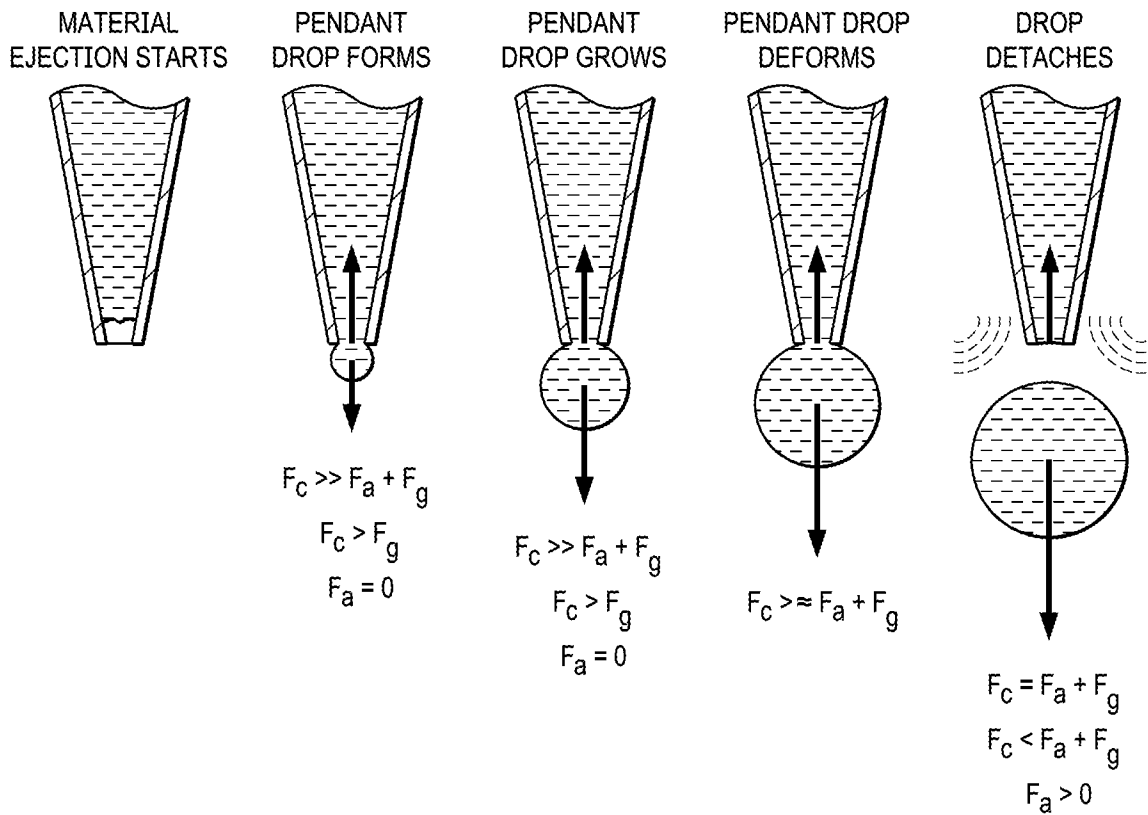


FIG. 4B



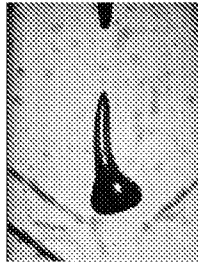


FIG. 5A



FIG. 5B

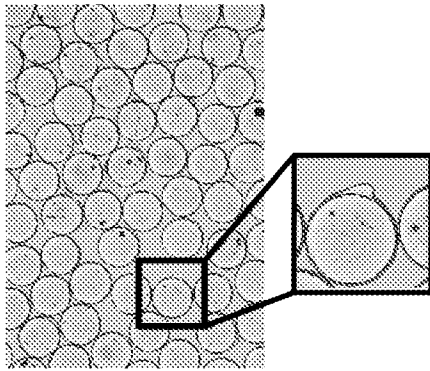


FIG. 5C

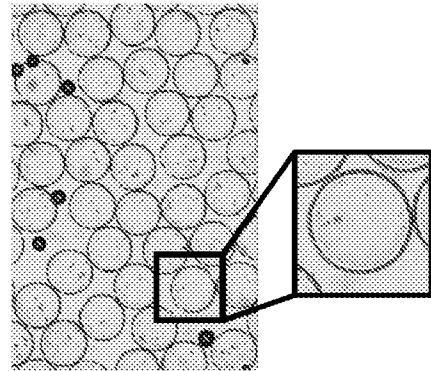
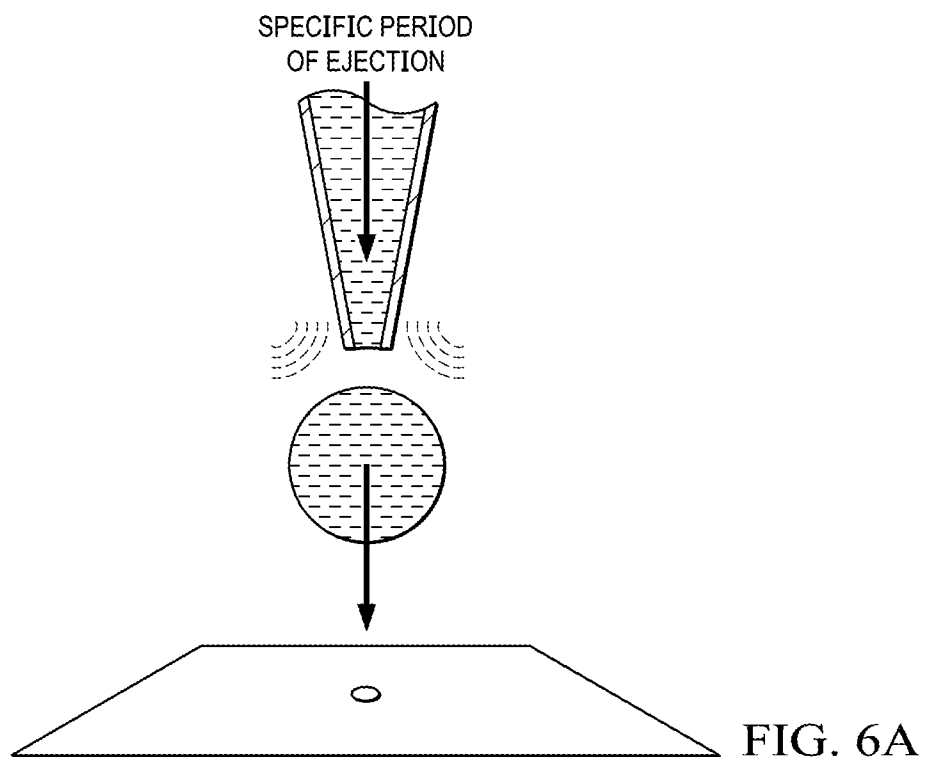
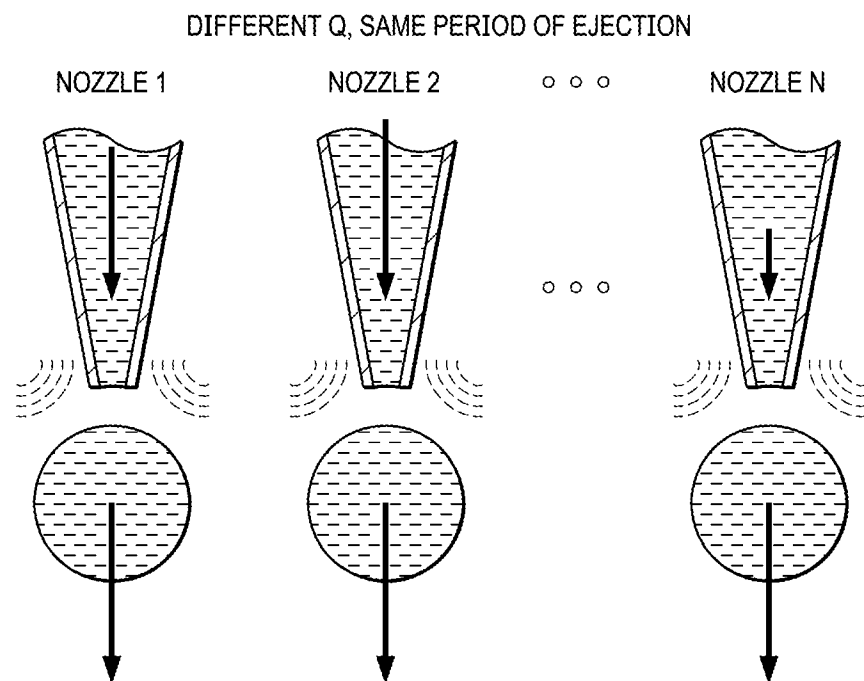
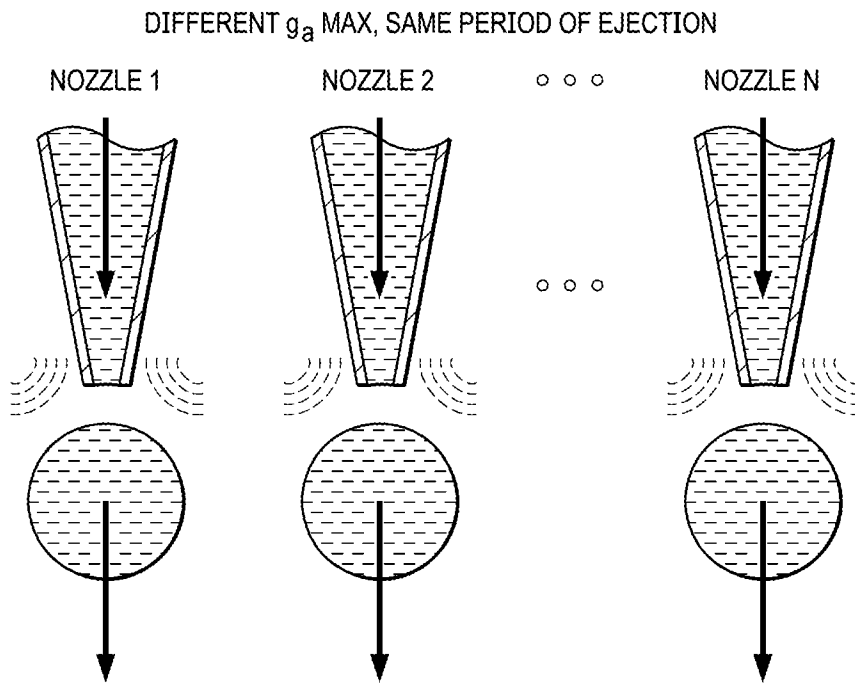
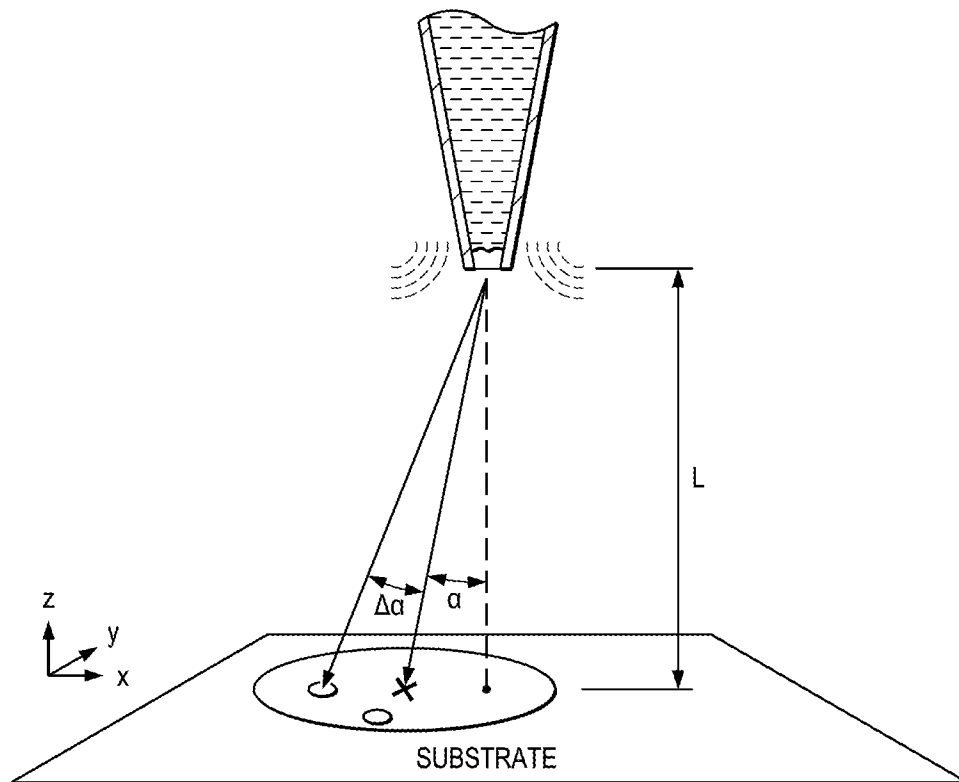


FIG. 5D







FROM α TO ε

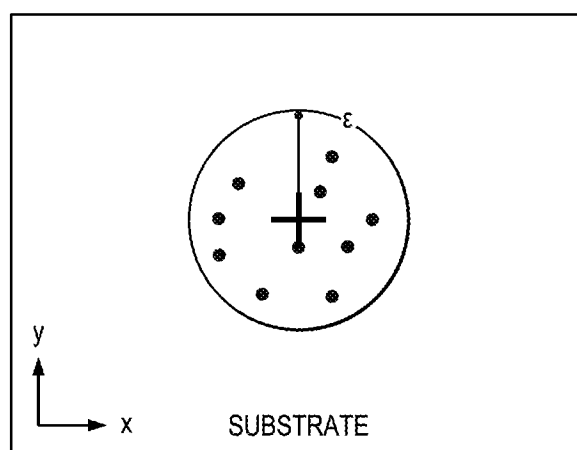


FIG. 7

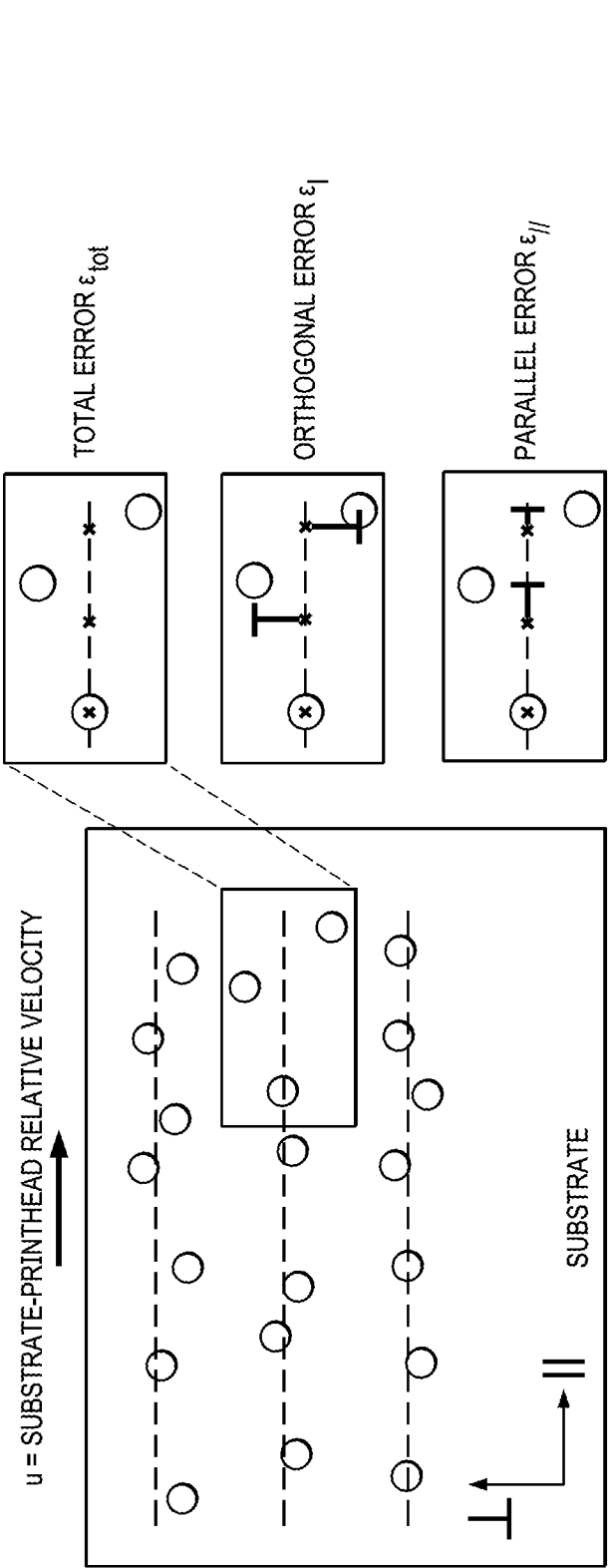


FIG. 8

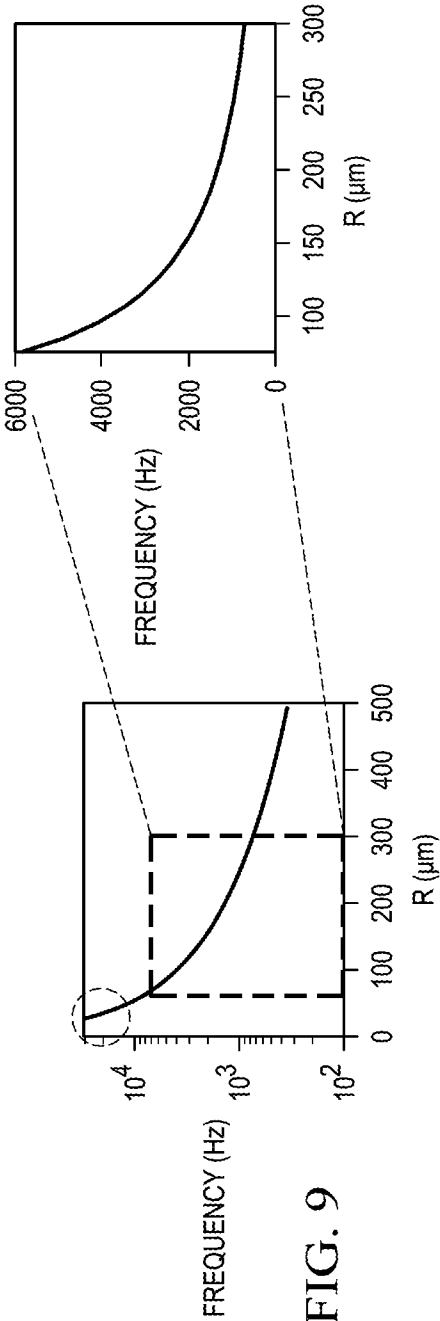


FIG. 9

FIG. 10A

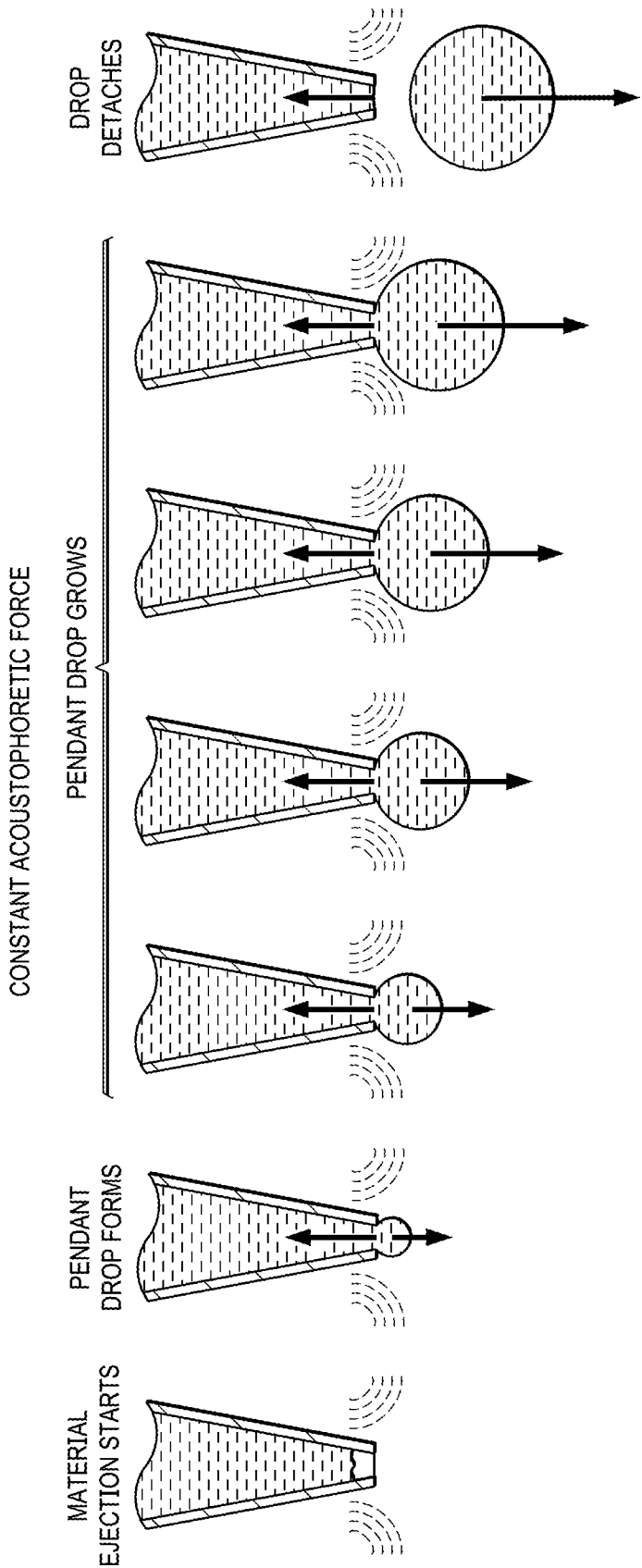


FIG. 10B

AMPLITUDE MODULATION OF ACOUSTOPHORETIC FORCE

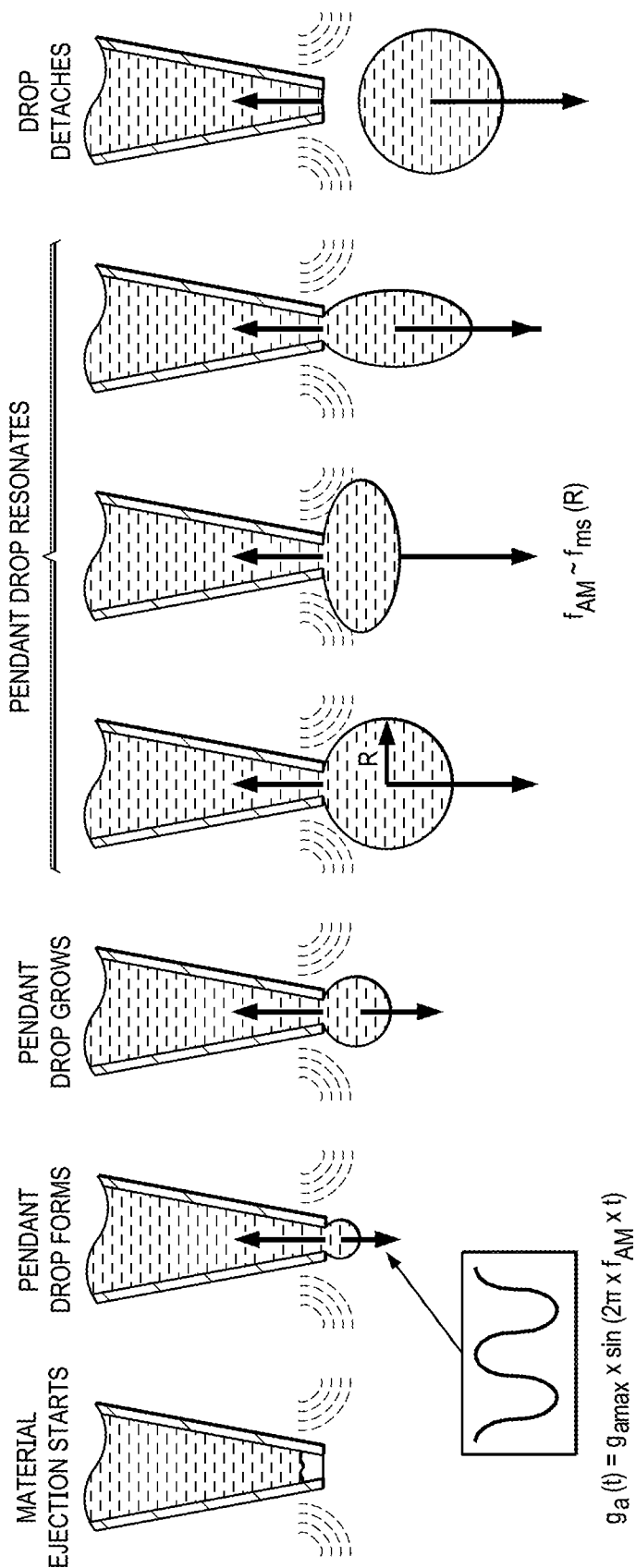
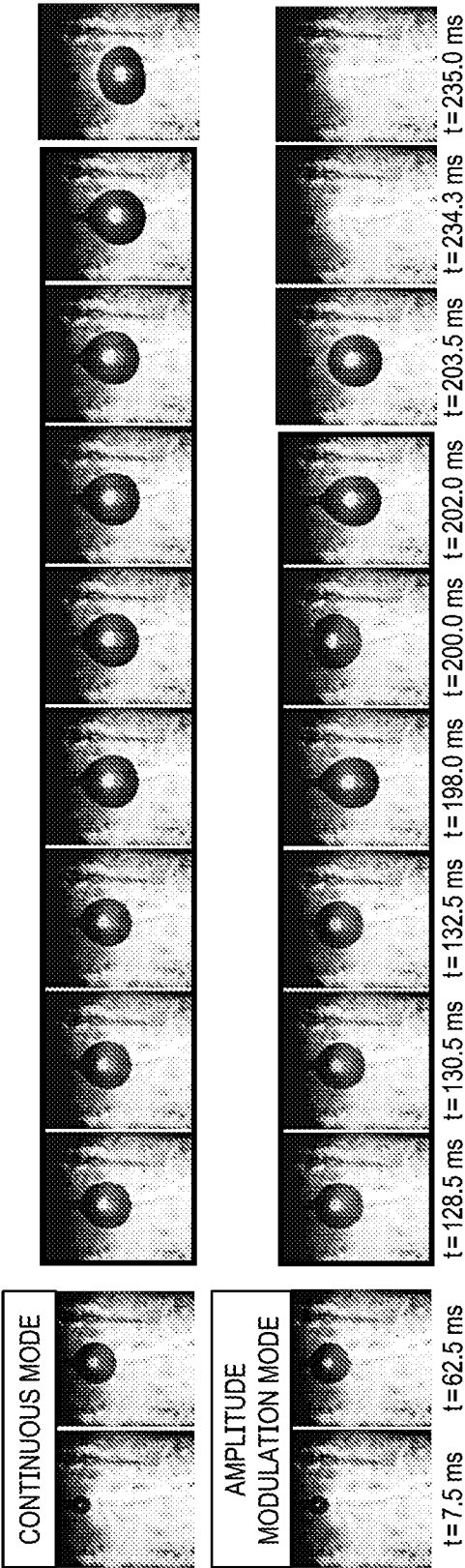


FIG. 10C



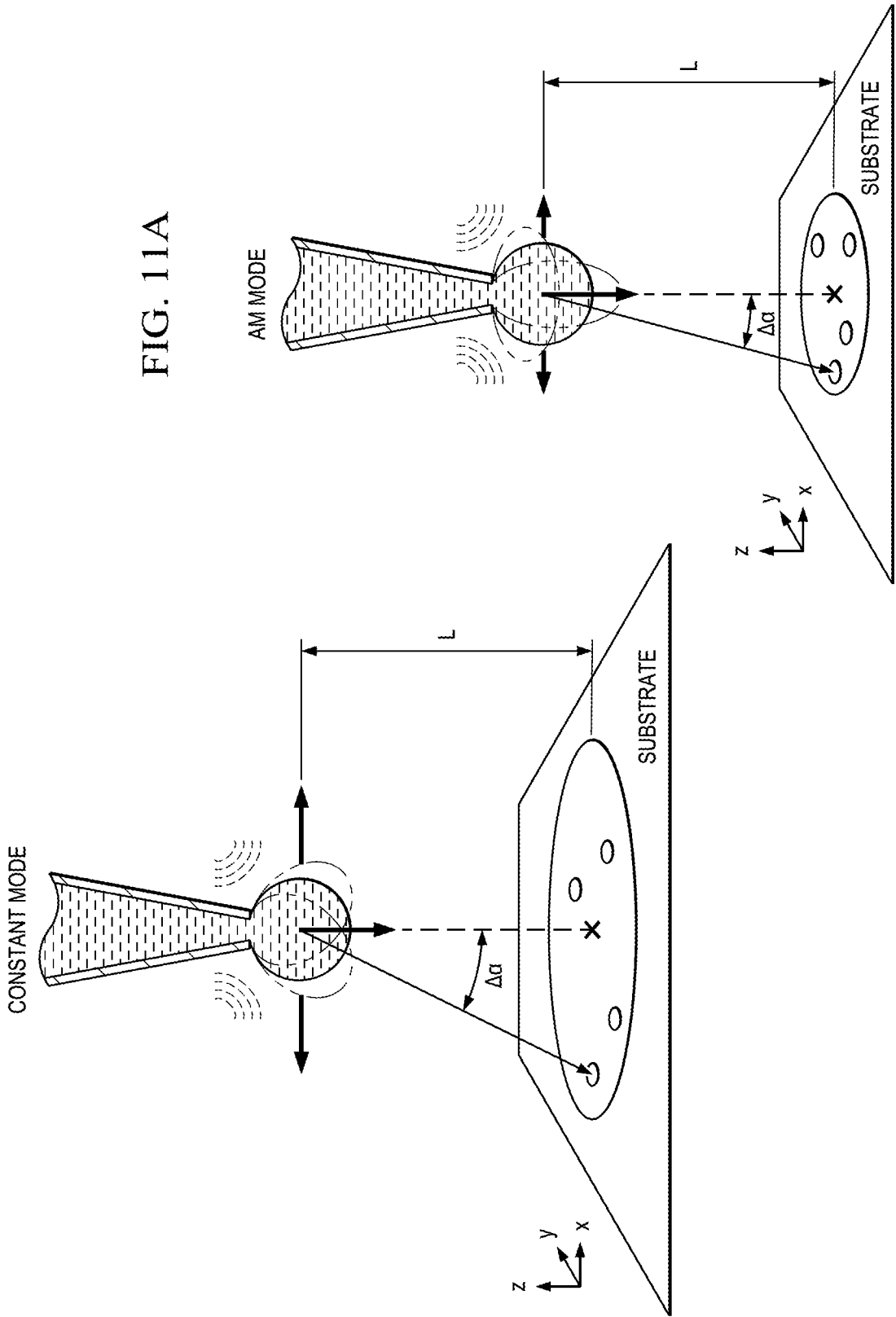
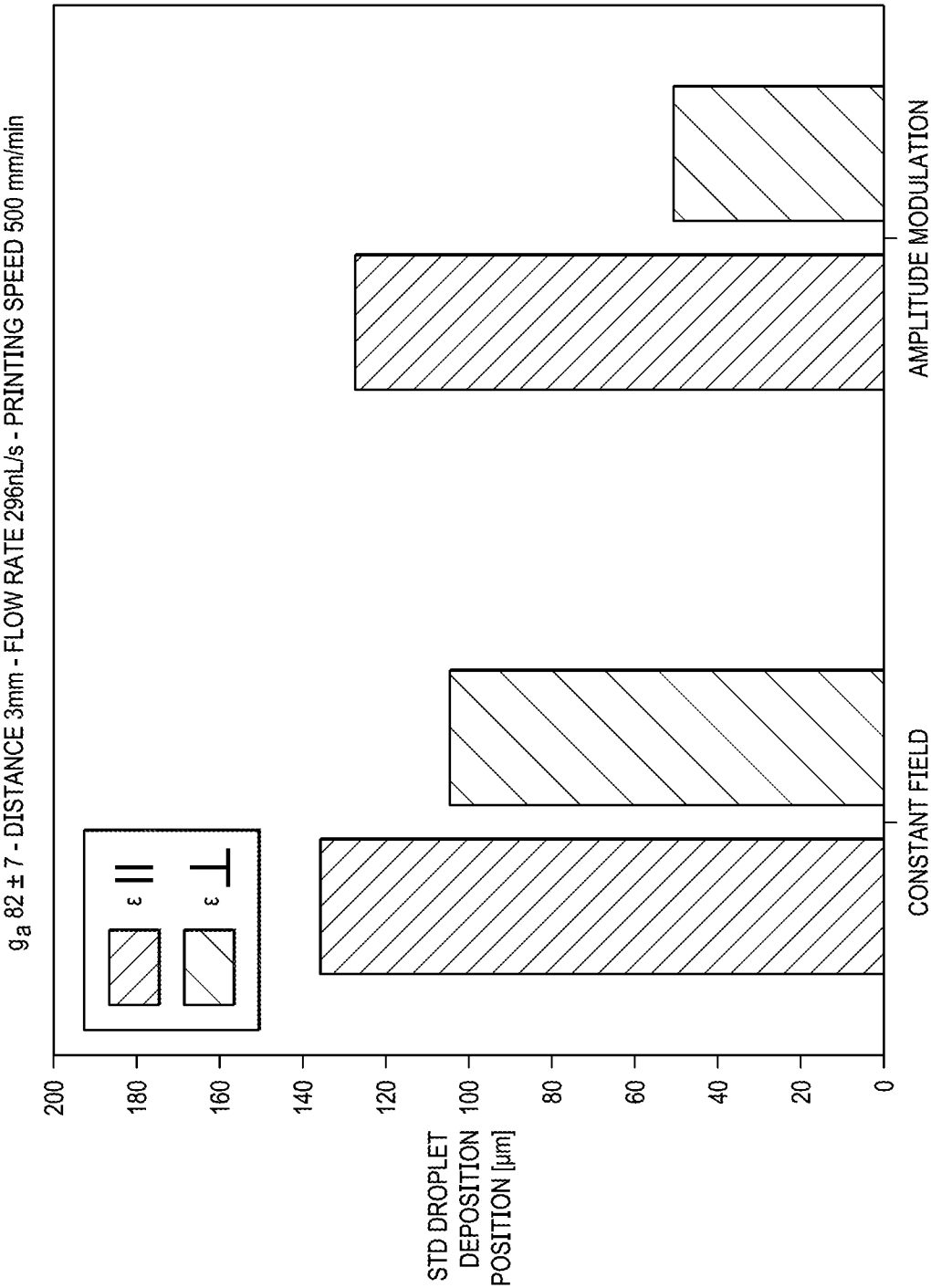


FIG. 11B



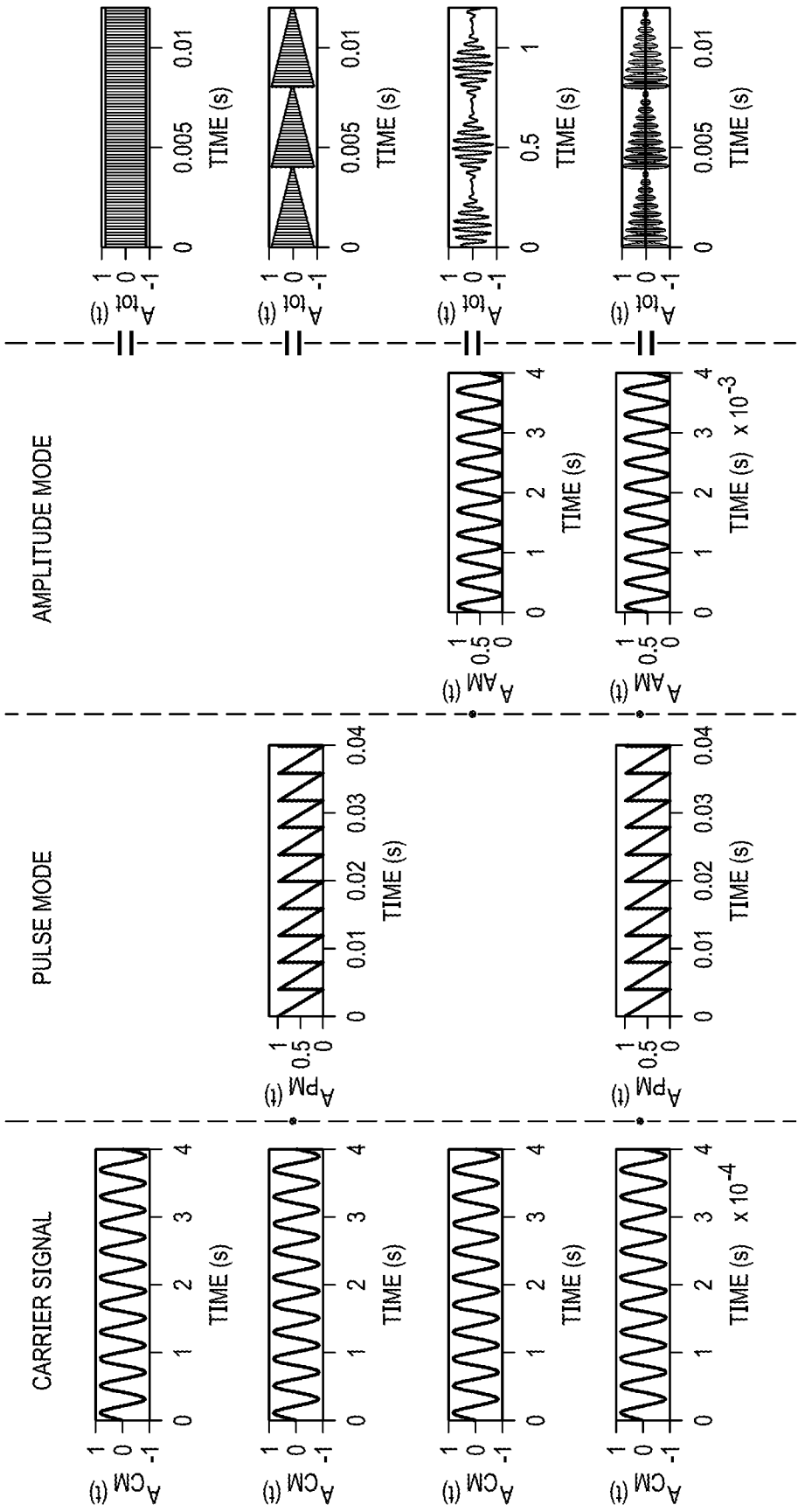


FIG. 12

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/29039

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B29C 64/112, B33Y 10/00, B33Y 30/00, B41J 2/14 (2019.01)
 CPC - B29C 64/112, B33Y 10/00, B33Y 30/00, B41J 2/14008

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2017/0001439 A1 (ETH ZURICH) 05 January 2017 (05.01.2017), para [0015], [0018], [0031], [0033], [0062], [0122]	1-4
A	US 5,138,333 A (BARTKY et al.) 11 August 1992 (11.08.1992), entire document	1-4
A	US 2005/068353 A1 (NISHIWAKI et al.) 31 March 2005 (31.03.2005), entire document	1-4

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

19 July 2019

Date of mailing of the international search report

30 JUL 2019

Name and mailing address of the ISA/US

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Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/29039

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 5-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.