Modeling of non-Newtonian suspension plasma spraying in an inductively coupled plasma torch

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Suspension plasma spray (SPS) is a promising technique for nano-structured coatings and nano-powder synthesis where nanoparticles are injected into the plasma jet with the help of liquid precursors. Most of the suspensions used in plasma spraying have the non-Newtonian behavior (viscoelastic or thixotropic). After injection into the plasma, the suspension is firstly atomized by the plasma jet before the droplets begin to vaporize. Understanding the breakup process of non-Newtonian liquid is critical to predict the condition of the resultant plasma spray. In this paper, a non-Newtonian liquid primary atomization model and a nanoparticle model are implemented into a radio frequency inductively coupled plasma model of suspension plasma spraying. After validation of the non-Newtonian liquid breakup models with the published experimental data, the comprehensive particle model is used to predict the trajectory, velocity, temperature and size of the in-flight nano- or agglomerate particles. The effects of the atomization operating conditions and the characteristics of the non-Newtonian liquid on the particle acceleration and heating process are investigated. The parameters that have a significant influence on the spray process are identified.

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1. Introduction

Suspension plasma spray (SPS) is a promising technique for nano-structured coatings and nano-powder synthesis [1–4], which allows the controlled injection of much finer particles than in conventional thermal spraying. In SPS, liquid fragmentation is a critical process since the injected suspension is firstly atomized into dispersed droplets by the plasma jet before the vaporization of the liquid carrier. The drops fragmentation size and velocity determine the subsequent heating and vaporization rates, ultimately the quality of the final product. While obtaining a controllable and efficient atomization effects is challenging in a plasma spraying system for at least two aspects. One is the complex physical properties of the liquid precursors. The suspensions formed by the nano-size powder agglomerated and dispersed in a liquid carrier always have non-Newtonian behaviors, generally viscoelastic or thixotropic, and the physical properties of suspension varied in a wide range. The other is the high requirement of the atomization in SPS system. For obtaining ideal coating or particle morphologies, the underlying goal of atomization is to produce a narrow distribution of sizes centered about the target value which can be achieved by the traditional approach of increase in gas flow rate and reduction in exit orifice size. However, the velocity and flux of atomized gas should be minimized because a high gas flow rate will strongly disturb the plasma filed. In addition, for alleviating clogging problem, especially for high viscosity liquid, the exit orifice of nozzle should not be too small.

For the above concerns with the atomization process of SPS, on one hand it is necessary to have a fundamental understanding of the non-Newtonian liquid breakup mechanism. The ability to predict jet breakup from theory and modeling has been actively pursued by many authors. Sirignario and Mehring [5] reviewed the linear and nonlinear analyses of the instabilities and distortion of liquid stream injected into a gas media. Villermaux [6] reviewed the interpretations and paradigms of liquid fragmentation. Aliseda et al. [7] describes a collaborative theoretical and experimental research to investigate the atomization dynamics of non-Newtonian liquid in a coaxial atomizer. Xue et al. [8] used a two-dimensional computational approach to predict the effect of coupled surfactant and non-Newtonian mechanisms on the formation of satellite drops. For the atomization in the application of SPS, Bouyer et al. [9] firstly investigated the atomization process in thermal plasma chemical vapor deposition. Fazilleau et al. [4] proposed models to describe the interactions between plasma and suspension droplets. Fauchais et al. [1] reviewed the issues for drops and jet fragmentation and...
Nomenclature

\( A \)  magnetic vector potential, A H m\(^{-1}\)
\( a \)  acceleration of the liquid ligament, m s\(^{-2}\)
\( \text{ALR} \)  air-to-liquid ratio, by mass
\( B \)  magnetic flux density, T
\( C_p \)  specific heat, J kg\(^{-1}\) K\(^{-1}\)
\( C_d, C_d' \)  drag coefficient
\( D \)  diffusion coefficients, m\(^2\) s\(^{-1}\)
\( d_n \)  nozzle diameter, m
\( E \)  electric field, V m\(^{-1}\)
\( e \)  internal energy, J
\( f \)  frequency, Hz
\( F \)  Force, N
\( g \)  gravity force, N
\( H \)  magnetic field, A m\(^{-1}\)
\( h \)  heat transfer coefficient
\( J \)  current density, A m\(^{-2}\)
\( k \)  dimensional wave number, m\(^{-1}\)
\( K_n \)  Knudsen number
\( L_m \)  latent heat of fusion, J kg\(^{-1}\)
\( L_v \)  latent heat of evaporation, J kg\(^{-1}\)
\( m \)  mass, kg
\( Nu \)  Nusselt number
\( P_p \)  pressure, kg m\(^{-2}\) s\(^{-2}\)
\( Pr \)  Prandtl number
\( Q_j \)  Joule heating, W m\(^{-3}\)
\( Q_{\text{conv}} \)  convection heat, W m\(^{-3}\)
\( Q_{\text{rad}} \)  radiation heat loss, W m\(^{-3}\)
\( Q_{\text{vap}} \)  vaporization heat, W m\(^{-3}\)
\( q \)  heat flux, W m\(^{-3}\)
\( R \)  radius, m
\( Re \)  Reynolds number
\( Sh \)  Sherwood number
\( Sc \)  Schmidt number
\( Sr \)  interface velocity slip ratio
\( SMD \)  Sauter mean diameter, m
\( r \)  radial coordinate, m
\( t \)  time, s
\( T \)  temperature, K
\( T_e \)  un-relaxed axial time, s
\( u, v, w \)  velocity component, m s\(^{-1}\)
\( x \)  axial coordinate, m
\( \Delta \)  effective shear viscosity, Pa s
\( \mathbb{R} \)  non-dimensional wave number

Greek symbols

\( \alpha \)  volume fraction
\( \delta_{\text{lg}} \)  ligament thickness, m
\( \phi_1 \)  measures of viscoelasticity
\( \zeta \)  inertial forces relative to surface tension forces
\( \gamma \)  non-dimensional growth rate
\( \eta \)  viscosity, Pa s
\( \eta_0 \)  zero shear viscosity, Pa s
\( \lambda_1 \)  fluid relaxation time, s
\( \lambda_2 \)  fluid retardation time, s
\( \mu_0 \)  permeability in vacuum, 4\( \pi \times 10^{-7}\) H m\(^{-1}\)
\( \theta \)  azimuthal coordinate
\( \rho \)  density, kg m\(^{-3}\)
\( \sigma \)  liquid surface tension, kg m\(^{-2}\)
\( \xi \)  specific heat ratio
\( \tau \)  electrical conductivity, s m\(^{-1}\)
\( \omega \)  angular frequency, rad s\(^{-1}\)
\( \vartheta_p \)  melt fraction of the particle

Superscripts

-  flow ratio
—  mean

Subscript

\( c \)  cell
\( f \)  film surrounding particle surface
\( g \)  gas
\( \text{ind} \)  induce
\( l \)  liquid
\( o \)  orifice
\( p \)  particle
\( \text{rel} \)  relative
\( s \)  sheet
\( \text{so} \)  solid
\( \text{sl} \)  solvent
\( v \)  vapor
\( w \)  vicinity of the particle surface

Concluded the effective parameters. Qian et al. [10] simulated the outflow of the effervescent atomization spray for various Newtonian liquid under normal temperature.

On the other hand, it is essential to choose a robust spray system which can meet the requirements of suspension plasma spraying. Compared to other conventional pressure, rotary or twin-fluid atomizers, effervescent atomization, a method of twin-fluid atomizers, offers that involving bubbling gas directly into the liquid stream internally, which can meet the requirements of suspension plasma spraying. Newtonian liquid under normal temperature.

Sojka and co-workers [11–14] reviewed the fundamental research about the basic mechanisms as well as the investigation of atomizer performance. Recently, Esfarjani and Dolatabadi [15] numerically investigated the two-phase flow inside an effervescent atomizer for the suspension plasma spray. Qian et al. [16] numerically studied the evolution of drops in the suspension plasma spray for a radio frequency (RF) torch. However, for suspension plasma spray, the breakup mechanism of non-Newtonian liquid jet has not been reported yet.

The present work is devoted to establishing the breakup model of non-Newtonian liquids using a ligament formation assumption with two dispersion relationships proposed by Goren and Gortfleib [17] and Joseph et al. [18] respectively. This two breakup model will be validated and compared with published experimental data. Then, the non-Newtonian liquid primary atomization model as well as a nano-particle model is implemented into a radio frequency inductively coupled plasma model to explain the suspension plasma spraying. The atomized droplets with suspended powder are tracked in a Lagrangian manner, including the solvent evaporation, nano-particles and agglomerates discharge, heating and evaporation. In the nano-particle model, non-continuum effects on particle acceleration and heating, known as Knudsen effects, are considered, as well as the influence of evaporation on the heat transfer. The effects of gas properties, thermodynamic and transport [19,20] on particle momentum and heating transfer characteristic are modeled [21,22]. Finally, the comprehensive particle model is used to predict the trajectory, velocity, temperature and size of the in-flight nano- or agglomerate particles. The effects of the atomization operating...
conditions and the characteristics of the non-Newtonian liquid on the particle acceleration and heating process are investigated. The parameters that have a significant influence on the spray process according to our model are presented.

2. Basic description

In the present study, the suspension plasma spray system is based on a radio frequency induction plasma torch system (PL-50 model, Tekna Inc.) with an effervescent atomizer for the suspension spray. Details of the principal dimensions of the torch, identified in Fig. 1, are given in Table 1.

As shown in Fig. 2, in suspension plasma spray, the liquid precursors containing nano-size powders are firstly fragmented by the jet into dispersed droplets which can be named primary atomization. After primary atomization, droplets secondary atomization and collision are two possible momentum events in the spray field. While in RF plasma flow field, the secondary atomization almost never occurs because the relative velocity of gas and droplet are always below 100 m/s [1]. Furthermore, as studied by Ref. [16], the effects of droplet collision and coalescent events on the final particle characteristic are not significant under normal operating conditions. Therefore, with temperatures in the order of 10,000 K, the dominant events of the atomized droplets in a RF plasma jet. Finally, the nano- or agglomerate particles will experience further heating, melting or even evaporation before chemical synthesis or impinging onto the substrates.

3. Non-Newtonian liquid primary atomization

Supported by high-speed photographs [12], the flow structure near the nozzle exit is firstly annular pattern during the primary breakup. Secondly the annular liquid sheath is shattered into a number of cylindrical ligaments by the rapidly expanding gas phase, then the ligaments break into ligament fragments. Thus, the primary atomization model can be established on the following assumptions:

- i The annular two-phase flow within the discharge orifice is one-dimensional, inviscid and isothermal with compressible ideal gas and small interface velocity slip ratio.
- ii The annular sheath liquid breaks into a number of cylindrical ligaments with almost the same diameter as the thickness of the annular sheet.
- iii The ligaments breakup into ligament fragments at the wavelength of the most rapidly growing wave, the size of a typical ligament fragment can be determined with the linear instability analysis.
- iv Each ligament fragment is stabilized to one spheric droplet under the influence of surface tension. The schematic of effervescent atomization is shown in Fig. 1.

Based on the above descriptions, in the present atomization model the first step is estimation of the annular sheets as well as the cylindrical ligaments. The momentum equation of the annular flow can be written as the Bernoulli equation

$$\frac{dp}{\rho_g} + v_g dv_g = 0,$$

where $p$ is the gas inside pressure, $\rho_g$ is the gas density, $v_g$ is the gas velocity. Combined with the state equation, Eq. (1) can be integrated to

$$RT \ln \left( \frac{\rho_g RT}{\rho_l} \right) + \frac{1}{2} \left( \frac{m_l ALR}{\rho_g \pi r_g^2} \right)^2 = \text{const}$$

where $r_g$ is the radius of gas flow, $m_l$ is the mass flow rate of liquid, and ALR is the air–liquid ratio by mass. The radius of gas flow can be written in terms of orifice radius $r_o$ and void fraction $\alpha$, $r_g = \sqrt{\alpha r_o}$. The interface velocity slip ratio $v_{slip}$ under different flow rate is expressed as [23]

$$v_{slip} = \sqrt{\frac{p_l}{p_g} \frac{\sqrt{\alpha}}{1 + C (1 - \alpha)}},$$

where $C$ is the experimental coefficient of the mass flow rate scaling. The interface velocity slip ratio and void fraction are related by

$$1 + \frac{p_g sr}{\rho_l ALR} = \frac{1}{\alpha}$$

By solving Eqs. (2)–(4), $\rho_g$, $\alpha$ and $v_{slip}$ can be calculated for different operating conditions. The thickness of annular liquid sheet is then calculated from $h_{lag} = 4(r_o - r_g) / \sqrt{\pi}$, which is also the diameter of the typical cylindrical ligament.

Secondly, the formed ligaments can be approximated by cylindrical jets. The ligaments will breakup into ligament fragments at the wavelength of the most rapidly growing wave. In present study, two linear instability dispersion relationships proposed by Goren
Goren and Gortlieb (G&G) dispersion relationship is derived from the linearized stability analysis of surface tension driven breakup. Subjected to the boundary conditions at the interfaces between the liquid and gas, the dispersion relation of G&G was analytically obtained by solution of the linearized liquid continuity, momentum and constitutive equations for general visco-elastic fluid, on which the small disturbance are superimposed. The crucial idea of G&G’s contribution [17] is that they developed Weber’s Newtonian liquid linear stability analysis (Eq. (5)) by substituting the liquid viscosity \( \eta \) for \( \eta_0(1 + \gamma q)/[1 + \lambda \gamma q] \) and involving an un-relaxed tensile stress \( T_e \), which generates during extrusion and will retard the disturbance growth, to explain the stabilization of the visco-elastic jet. Goren and Gortlieb’s dispersion relation can be expressed by non-dimensional form as Eq. (6) [24]

\[
\gamma^2 + \frac{3\gamma k^2}{\bar{p}_l} - \frac{ak^2(1 - k^2\delta_{\text{lig}}^2)}{2p_l\delta_{\text{lig}}} = 0 \tag{5}
\]

\[
\zeta \gamma^2 + \frac{3\pi^2 \rho(1 + \phi_1 \gamma)}{(1 + \bar{\eta} \gamma)} - \frac{\pi^2(1 - \pi^2\eta^2)}{2} - T_e \pi^2(1 - \phi_1 \gamma) = 0 \tag{6}
\]

where \( \gamma \) is the non-dimensional growth rate, \( \zeta \) presents the inertial forces relative to surface tension forces, \( \zeta = 2\pi^2\eta_0 \gamma_0^2 \delta_{\text{lig}}^2 \) is the dimensional wave number of a disturbance, \( \eta_0 \) is the zero shear viscosity, \( \rho_l \) is the liquid density, \( \sigma \) is the liquid surface tension. \( \bar{\eta} = \delta_{\text{lig}} k/2\pi \) is the modified non-dimensional wave number, \( \phi_1 \) and \( \phi_2 \) are measures of viscoelasticity that include the fluid relaxation time \( \lambda_1 \) and retardation time \( \lambda_2 ; \phi_1 = 2\lambda_1 \sigma_0 / \eta_0 \delta_{\text{lig}} \), \( \phi_2 = 2\lambda_2 \sigma_0 / \eta_0 \delta_{\text{lig}} \). For a dilute polymer solutions, the relationship of retardation time and relaxation time is \( \lambda_2 = \lambda_1 \beta / \eta_{\text{solvent}} / \eta_{\text{solution}} \) [25]. \( \eta_{\text{solvent}} \) and \( \eta_{\text{solution}} \) are the viscosity of solvent and solution, respectively. \( T_e \) is the un-relaxed axial time normal to the direction of the flow which would cause the visco-elastic jet to be stabilized, as suggested by Bousfield et al. [26]. \( T_e \) can be expressed as

\[
T_e = 32(1 - \lambda_1 / \lambda_2) \left( \frac{2\lambda_1 \delta}{\delta_{\text{lig}}} \right)^2.
\]

where \( \overline{V}_l \) is the average velocity of the liquid. Then, Eq. (5) can be written as a fourth-degree polynomial in the growth rate \( \gamma \) and solved analytically. The restrictions of G&G dispersion relationship mainly from two aspects: one is G&G’s work considers for an unsteady but axisymmetric jet of visco-elastic liquid slowly moving through an inviscid gas. Therefore, the prediction of the dispersion relationships will deviate from the experiments when the gas—liquid relative velocity is high. The other is that when \( \phi_1 \gamma < 1 \), the growth rate predicted by Eq. (6) is reduced as the value of the un-relaxed axial tension decreases, which is unphysical.

Joseph’s dispersion relationship [18] is obtained from the Rayleigh-Taylor instability analysis. By taking the acceleration of a drop exposed to a high-speed air steam into account, the equations of motion coupled with boundary conditions are solved to deduce the expression of the disturbed interface. In present study, the ligament with thickness \( \delta_{\text{lig}} \) that grows rapidly and accelerated by explosion bubbles is similar to a flattened drop in a high-speed gas stream. Subjected to the Rayleigh-Taylor instability, the non-Newtonian fluids dispersion relation can be given as

\[
-1 + \frac{1}{\gamma^2} \left( -a_k^2 \bar{p}_l + \frac{ak^3}{\bar{p}_l} \right) - \frac{4k^2 \Delta}{\gamma^2 \bar{p}_l} + \frac{4\lambda_1^3 \Delta}{\gamma^2 \bar{p}_l} \sqrt{k^2 + \gamma \rho_1 / \Delta - k} = 0 \tag{8}
\]

Eq. (8) is an approximate analysis of Rayleigh-Taylor instability based on visco-elastic potential flow which gives the critical wavelength and growth rate to within less than 10% of the exact theory. In Eq. (8), \( \Delta \) is the magnitude of the wave number, \( \gamma \) the amplification rate, \( \sigma \) the liquid surface tension. \( \Delta \) the effective viscosity of the liquid, \( \Delta = \eta_0(1 + \lambda_2 \gamma)/[1 + \lambda_1 \gamma] \). For visco-elastic liquid, \( \Delta \) is large and \( \gamma \rho_1 / (k_0 \Delta) \ll 1 \), then \( (\sqrt{k^2 + \gamma \rho_1 / \Delta - k} \) can be assumed to be \( \gamma \rho_1 / 2\lambda_2 k_0 \). \( \gamma \) is the acceleration of the liquid ligament. Assumed that only the drag force affect the ligament momentum transfer with the atomization jet and the ligament can be considered as a flattened drop, the drag force exerted by the gas stream on a liquid element is \( F_{\text{drag}} = \gamma \rho_1 (u_0 - u)^2 A_0 / 2 \), where \( A_0 \) is the projected area, \( \gamma \) is the drag coefficient. As the ligament Reynolds number: \( \text{Re}_{\text{lig}} = \gamma \rho_{\text{lig}} \overline{V}_l \delta_{\text{lig}} / \mu_0 \) is between 3 and 1000, here \( \gamma = 24(1 + \text{Re}_{\text{lig}}^{2/3}) / \text{Re}_{\text{lig}} \). Considering the liquid ligament mass \( m = \gamma \rho_{\text{lig}} \delta_{\text{lig}} \overline{V}_l \), then \( a \) can be written as: \( a = \gamma \rho_1 (u_0 - u)^2 / (\gamma \rho_{\text{lig}}) \). Then, Eq. (8) reduces to a three-degree polynomial of \( \gamma \) and can be solved analytically. As considering the high relative velocity between the gas and liquid, Joseph’s dispersion relation is more reasonable than that of G&G for atomization jet. While Joseph’s work is based on the assumption of a flattened drop, the divergence may occur when the liquid ligament is not similar to a flattened drop.

Based on above two dispersion relations, the critical breakup wave number that corresponds to the maximum growth rate can be used to calculate the wavelength of a typical ligament fragment. Finally, assuming that each fragment is stabilized to one spherical droplet under the influence of surface tension, the Sauter mean drop diameter SMD (defined as the ratio of volume-to-surface area) can then be calculated from the conservation of mass

\[
\text{SMD} = \left[ \frac{3\pi \delta_{\text{lig}}^2}{k_0} \right]^{1/3}.
\]

### 4. Particles model

In present study, particle means the computational particle (parcel) or discrete Lagrangian entities, which can stand for droplets and also solid particles. A computational particle (parcel) is consisted of a number of droplets/solid particles with same physical properties and behaving equally. After primary breakup, the atomized droplets contained nano-particles are treated as a discrete Lagrangian entity. Only the viscous drag forces are taken into consideration, due to the particle diameter is less than 100 \( \mu m \) [27]. The momentum transfer between the particle and the plasma can be described by
\[
\vec{F}_p = m_p \frac{d\vec{V}_p}{dt} = \pi r_p^2 C_D \frac{\rho_l |\vec{V}_g - \vec{V}_p| (|\vec{V}_g - \vec{V}_p|)}{2}
\]

(10)

where \( \vec{V}_g \) is the gas velocity, \( C_D \) is the drag coefficient, which includes the influence of the local temperature and heat transfer coefficient of the plasma gas around the particles and can be expressed as

\[
C_D = \left( \frac{24}{Re_p} + \frac{6}{1 + \sqrt[4]{Re_p}} + 0.4 \right) f_{prop} f_{Kn}^{0.45}
\]

(11)

Here the particle Reynolds number, \( Re_p \), is defined as \( 2 \rho_p |\vec{V}_g - \vec{V}_p|/\mu_g \). \( f_{prop} \) represents the effect of variable plasma properties: \( f_{prop} = \rho_{eq} / \rho_{wv} \), \( f_{Kn} \) indicates the influence of non-continuum [28]

\[
f_{Kn} = \left[ 1 + \left( \frac{\zeta_w}{1 + \zeta_w} \right) \frac{6}{Pr_w} \right]^{Kn}
\]

(12)

where \( \zeta \) and \( Pr \) are the specific heat ratio and the Prandtl number of the plasma gas. The subscript \( w \) presents the vicinity of the particle surface. \( Kn \) is the Knudsen number based on the effective mean free path. The momentum transfer of both suspension droplets and nano-particles with the plasma jet are calculated in the same way. While, the size effect is presented by the Knudsen number, \( f_{Kn} \), which has values of 0.005–0.1 for nano-particles and 0.994–0.996 for suspension droplets.

4.1. Suspensions heating

The main phenomenon for suspension droplet in a radio frequency plasma spray is the solvent heating and evaporation [1] which depends on the information of the droplet external conditions determined by the plasma gas. Due to the low Biot number (defined as the ratio of convective to conductive heat transfer), the temperature distribution in the particle is assumed to be uniform and the lumped heat capacity model is used for both the suspension and solid particle heating process. The evolution of the droplet temperature can be expressed by [29]

\[
\begin{align*}
T_d &= T_{d0} + \frac{Q_d}{m_d c_{pd}} \text{ if } T_d < T_{vd} \\
T_d &= T_{vd} \text{ if } m_d c_{pd} (T_{vd} - T_{d0}) + m_d a_g L_V
\end{align*}
\]

(13)

where \( T_{d0}, Q_d, m_d, c_{pd} \) are the initial temperature, heat gain, mass, and the specific heat of the droplet, respectively. The specific heat of the droplet, \( c_{pd} \), is averaged based on the mass fraction as \( c_{pd} = c_{pd} (1 - \alpha) + c_{pd} \alpha \). The subscript \( v \) represents vaporization. It is assumed that the solid particles are suspended randomly inside the droplet. As illustrated in Fig. 2, once the solvent is totally vaporized, the solid particles containing in the suspension are discharged into the plasma jet. The solid particles might explode to smaller pieces of agglomerates or individual nano-particles. These single nano-particles and agglomerate particles are treated as new Lagrangian entities with the current parameters of position, droplet velocity and temperature.

4.2. Solid particles heating and mass transfer

Based on lumped heat capacity model, the nano- or agglomerate particle energy conservation equation can be expressed as

\[
m_p c_p \frac{dT_p}{dt} = \pi D_p^2 \frac{q_p}{\varphi_p} \text{ (for } T_p \neq T_m)\]

(14)

\[
m_p m_p c_p \frac{d\varphi_p}{dt} = \pi D_p^2 \varphi_p q \text{ (for } T_p = T_m)\]

(15)

where \( \varphi_p \) is the melt fraction of the particle and \( q \) is the heat flux at the particle surface. If considering heat transfer by convection, evaporation and radiation, \( q \) can be express as: \( q = Q_{conv} - Q_{vap} - Q_{rad} \), in which \( Q_{conv} \) is convective heat transfer: \( Q_{conv} = 4\pi r_p^2 h(T_f - T_s) \), \( Q_{vap} = m_f h_{evp} \) is the vaporization of heat transfer, \( \varphi_p = 4\pi r_p^2 \rho \sigma (T_f^4 - T_s^4) \) is the heat loss due to radiation. The film temperature \( T_f \) is introduced to deal with the steep temperature gradient in the boundary layer around the particle and defined as the average value of gas temperature at the cell where the particle is located and the immediate vicinity by the particle surface: \( T_f = (T_g + T_s)/2 \). The heat transfer coefficients \( h \) can be calculated from the Nusselt number \( Nu = 2h r_p / k_f = (2 + 0.6 Re_p^{1/2}) Pr_1^{1/3} / f_{rop} f_{Kn} f_{w} \), where \( f_{Kn} \) and \( f_{rop} \) are defined in Eq. (11), \( f_w \) accounts for the effect of mass transfer due to evaporation [16]. \( f_r \) approaches one when the evaporation mass rate \( m_w \) is close to zero, \( f_r \) is smaller than one when \( m_w \) is larger than zero. This indicates that the convective heat flux becomes smaller when accounting for the evaporation.

In present study, a model that can consider vaporization at any temperature is used [28]. The evaporation mass rate \( m_w \) is controlled either by the vapor diffusion or the heat transfer through the boundary layer around the particle. The evaporation rate is limited by the minimum of the vapor diffusion rate and the net heat gain of the particle as follows:

\[
m_w = \min \left\{ \left( 2 \pi D \right) \frac{v}{\zeta} \pi \right\} \varphi_p q \text{, } Q_{conv} - Q_{rad} / L_v \},
\]

(16)

where \( D \) is the diffusion coefficient, \( Sh \) is the Sherwood number representing convective mass transfer \( Sh = (2.0 + 0.6 Re_1^{1/2}) Pr_1^{1/3} f_{rop} f_{Kn} f_{w} \). \( Sc \) is the Schmidt number: \( Sc = \mu_f / (\pi D) \). In Eq. (16), the mass transfer number \( \zeta \) is related to the local mass fraction of vapor in the gas phase \( (Y_v) \) and the vapor concentration on the droplet surface \( (Y_r) \), defined as \( \zeta = (Y_r - Y_v)/(1 - Y_v) \) [16].

5. Plasma model

The mathematical modeling used for calculating the flow and temperature distribution of RF plasma field should consider two parts: the Maxwell equation for the electromagnetic field and the transport equations for the thermo-fluid field. The electromagnetic field interacts simultaneously with the thermo-fluid field. The RF plasma is sustained by receiving the electromagnetic energy from the induction heating system.

The RF plasma model is based on the following assumptions:

i. The flow field is steady, laminar and axisymmetric, electromagnetic field is quasi-steady and axisymmetric.

ii. Axial component of the coil current is negligible, the viscous dissipation and the pressure work in the energy equation are negligible, the displacement current term associated with an oscillating electric field is neglected in Maxwell’s equations.

iii. The plasma is local thermodynamic equilibrium (LTE) and optically thin.

The governing equations of mass, momentum, energy and species concentrations, as well as the vector potential form of Maxwell equations are in that case as follows:

\[
\frac{\partial}{\partial x}(\rho u) + \frac{1}{r} \frac{\partial}{\partial r} (r \rho v) = 0.
\]

(17)

Momentum conservation:
In Eq. (18), $F_x$ and $F_r$ are the momentum source terms due to Lorentz force at the axial and radial directions, $F_r = \mu_0 r \text{Re}(E_B \overline{H}_z)/2$. $F_x = -\mu_0 r \text{Re}(E_B \overline{H}_r)/2$, where $E_B$ is the tangential component of electric field intensity: $E_B = -\text{Im} \overline{H}_z$ and $H_r$ are the axial and radial component of magnetic field, respectively: $\mu_0 H_r = (1/r) \partial (r \text{Im} \overline{H}_z)/\partial r$. In Eq. (19), $Q_e$, $Q_i$ and $Q_{rad}$ are the energy source terms due to chemical reaction, Joule heating and radiation, respectively. $Q_i$ can be calculated from $Q_i = \tau E_B E_B/2$. In Eq. (21), $J_{\text{coil}}$ is the current in the coil, and $J_{\text{ind}}$ is the induced current in the plasma, which can be calculated from Ohms law: $J_{\text{ind}} = \tau E = -\text{Im} \overline{H}_z$. The plasma is assumed optically thin; therefore the radiant heat loss is treated as temperature-dependent volumetric sink term. In Eq. (20), $\mu_i e$ indicates different species and $\mu_i$ is the rate of density change due to chemical reaction. For the current study of argon plasma, the species include Ar and Ar$^+$, and an equilibrium reaction algorithm for the argon ionization and recombination is used [21].

### 6. Numerical setup

For the plasma filed, the governing equations of the velocity, temperature and species concentration are solved using the SIMPLE algorithm [30]. The computational simulations were performed on a cylindrical domain. The radius and axial lengths of the computational regime are 2.5 cm and 20 cm, respectively, while 2π in the circular direction. The mesh size is 120 (radial) × 160 (axial) × 32 (azimuthal). The grids in axial and radial directions are uniform staggered. The computational domain for the electromagnetic field is extended to the outside of plasma region. The axial and radial lengths of the computational regime are 1160 cm and 200 cm, respectively, using the non-uniform 282 × 175 grids in axial and radial directions respectively. Finer meshes are used for the core region of the electromagnetic field. The calibration of the plasma model and the validation of the gird dependency have been established in Ref. [14].

The boundary condition of the electromagnetic field and the flow field are similar to Ref. [14]. When the particles fly through the plasma flame, their mass, momentum and energy will dramatically change due to the interaction with the flame. The plasma gas equation will provide the gas information around the particles, while the effects of in-flight particles on the plasma are neglected due to the dilute spray system.

In the present computational frame, it is assumed that the suspension droplets are added into the gas phase randomly from the annular sheath of the atomizer exit after the gas phase reaches convergent solution. For each case, the total number of injected computational parcels is 10,000. The droplets are introduced in the

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Fig. 3. Initial distributions of solid particle size.

Fig. 4. Comparison of model prediction and experiment data [14].
system from the nozzle 1 at $x = 5$ cm (Fig. 1). The original size assigned to each droplet SMD is calculated from the primary breakup model with Rosin–Rammler distribution: $F_R = 1 - \exp\left(-\frac{D}{\text{SMD}_0}\right)^{q}$, where $q$ with the value of 5 indicated the value of the width of the distribution. The initial droplets velocity is the mean droplet velocity from primary breakup model with a random deviation within 5%; the direction with regard to injector axis is given by a random distribution from 0 to the cone angle of $5^\circ$; the droplet positions are randomly distributed in the exit plane of the annular liquid sheath. Therefore, multiple droplets have size, velocity, direction and position at the injection. Then, the suspension droplets load heating and evaporation, undergoing a series event of solvent evaporation, solid particles discharge, solid particle heating, melting and evaporation. Both the suspension droplet and the solid particles at all stages are tracked as discrete Lagrangian entity that exchanges mass, momentum, and energy with the plasma gas. The solid particles initial size distributions are shown in Fig. 3, which considered the typical size range for both nano-particles and agglomerates in suspension plasma spray.

7. Results and discussion

7.1. Effects on effervescent atomization

To validate the suspension primary breakup model, the experiments conducted by Geckler and Sojka [14] were simulated in which the radius of nozzle exit is 0.5 mm, the injection pressure is 3.5 MPa and ALR changes from 0.02 to 0.11. Both the dispersion relationships proposed by Goren and Gottlieb [17] (G&G) and Joseph et al. [18] are solved analytically. The predicted results and experimental data are compared in Fig. 4, in which “Model A” employed G&G’s linear analysis, and ”Model B” used Joseph’s. The experiments studied the effervescent atomization of visco-elastic fluids which are formulated by adding ethylene oxide to the composition of water and glycerin. The physical and rheological properties of the liquids [14] in Fig. 4 are listed in Table 2. As indicated by experiment, each data point in Fig. 4 is the average of three measurements with a mean statistical error of less than 0.5% and a maximum statistical error of 3.4%. The error bars are not included in Fig. 4 because the statistical deviation is smaller than the height of the symbols.

In Fig. 4 both the model A and B predict that with an increase in air-to-liquid mass flow ratio (ALR), droplet Sauter mean diameters will decline significantly, especially at lower ALR. The agreement between the predictions and measurements is qualitative achieved within 10–50% of experimental values for model A and within 5–20% for model B. The discrepancy is mainly due to three aspects. First, as pointed by Geckler and Sojka [14], as the experimental measurement of relaxation time is difficult, an approximately expression provided by Bird et al. [31] was used to estimate the relaxation time of polymer solution from polymer molecular weight in Geckler and Sojka [14]. The calculated relaxation time may differ from the measured value which will give rise to the inaccuracy of model prediction. Second, less gas fraction leads to bubbly flow and thus the assumption of annular flow is not applicable. Finally, the models have their auto-logous limitations. For example, the prerequisite of model B is the similarity between the ligament and a flattened drop, upon which Joseph’s linear Rayleigh-Taylor instability analysis can be used to determine the critical wavelength. While, at lower ALR, the ligament is slender, thus the model B prediction deviates from experimental data obviously. For model A, the shortcoming is that it provides unphysical results for weakly elastic fluids whose relaxation time is small enough to satisfy $\phi \gamma \ll 1$ [14]. Thus, the mean drop size predicted for the 0.001% solution is larger than that predicted for the 0.01% solution at lower ALR. Furthermore, compared the two mathematical models, model B with the dispersion relationship proposed by

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Baseline operating conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>Values</td>
</tr>
<tr>
<td>Liquid mass flow rate</td>
<td>2.2 g/s</td>
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<tr>
<td>Nozzle exit diameter</td>
<td>3 mm</td>
</tr>
<tr>
<td>Inject pressure</td>
<td>0.35 MPa</td>
</tr>
<tr>
<td>$Q_g$, carrier gas, Ar</td>
<td>6 SLM</td>
</tr>
<tr>
<td>$Q_c$, central gas, Ar</td>
<td>7 SLM</td>
</tr>
<tr>
<td>$Q_s$, sheath gas, Ar</td>
<td>30 SLM</td>
</tr>
<tr>
<td>ALR</td>
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</tr>
<tr>
<td>Inlet temperature</td>
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</tr>
<tr>
<td>Torch pressure</td>
<td>300 Torr</td>
</tr>
<tr>
<td>Coil current frequency</td>
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</tr>
<tr>
<td>Coil input power</td>
<td>33 KW</td>
</tr>
<tr>
<td>Expansion angle of spray</td>
<td>$5^\circ$</td>
</tr>
<tr>
<td>Content of solid, wt%</td>
<td>15%</td>
</tr>
<tr>
<td>Viscosity of solvent, mPa-s</td>
<td>1</td>
</tr>
<tr>
<td>Zero shear viscosity of suspension, mPa-s</td>
<td>25</td>
</tr>
<tr>
<td>Relaxation time, s</td>
<td>1.0e-4</td>
</tr>
</tbody>
</table>

SLM means standard liter per minute; 1 SLM = 16.67 cm$^3$/s.

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Solid particle and solvent physical properties.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspension content</td>
<td>Solid</td>
</tr>
<tr>
<td>Material</td>
<td>$\text{ZrO}_2$</td>
</tr>
<tr>
<td>Surface tension, $10^{-3}$ J/m$^2$</td>
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</tr>
<tr>
<td>Density, kg m$^{-3}$</td>
<td>$5.9 \times 10^3$</td>
</tr>
<tr>
<td>Solid thermal conductivity, W m$^{-1}$K$^{-1}$</td>
<td>2.0</td>
</tr>
<tr>
<td>Liquid thermal conductivity, W m$^{-1}$K$^{-1}$</td>
<td>3.0</td>
</tr>
<tr>
<td>Solid specific heat, J kg$^{-1}$K$^{-1}$</td>
<td>580</td>
</tr>
<tr>
<td>Liquid specific heat, J kg$^{-1}$K$^{-1}$</td>
<td>713</td>
</tr>
<tr>
<td>Melting temperature, K</td>
<td>2950</td>
</tr>
<tr>
<td>Boiling temperature, K</td>
<td>5000</td>
</tr>
<tr>
<td>Latent heat of melting, J kg$^{-1}$</td>
<td>$8 \times 10^3$</td>
</tr>
<tr>
<td>Latent heat of vaporization, J kg$^{-1}$</td>
<td>$6 \times 10^3$</td>
</tr>
</tbody>
</table>

Fig. 5. SMD versus ALR for various operating conditions and liquid properties.
Joseph et al. is more effective to capture the influence of rheological properties in the breakup process of non-Newtonian liquids and to quantitatively predict the resulting droplet sizes. One explanation is the relative velocity or acceleration between the gas and liquid is not considered in G&G’s dispersion relation, which is approximately correct only in the case of long wave disturbances. In the following investigations, model B will be used to simulate the suspension primary atomization.

As the atomization performance provides the initial conditions for heating process, it is important to see how sensitive the drop initial size is to change for various atomizer operating conditions and liquid rheological properties. The suspension feeding is prepared by dispersing the powders (metal, ceramic, biomaterial) with sizes ranging from 30 nm to 200 nm [16] in a liquid carrier (ethanol or water or a mixture of both), which always has non-Newtonian behavior, generally viscoelastic or thixotropic. The key physical properties of the visco-elastic liquid are: zero shear viscosity, relaxation time, viscosity of solvent, surface tension, density. For the effervescent atomizer, the main operating conditions are: gas-to-liquid mass flow ratio, injection pressure, nozzle orifice diameter, liquid mass flow ratio. Data for the baseline operating conditions and suspension physical properties are presented in Tables 3 and 4, respectively.

Fig. 5 analyzed the priorities of operating conditions and liquid properties to the droplet atomization. All the cases have the same operating conditions listed in Tables 3 and 4, except the specified condition in the legend of Fig. 5. It can be seen that increase of ALR has the most impact on the decrease of initial atomized droplet size. This is because larger gas flow rate and/or smaller liquid flow ratio lead to finer primary breakup and larger ALR indicates large velocity difference between the gas and liquid phases, which enhance the drop distortion and breakup. Besides ALR, larger nozzle exit size $D_{\text{noz}}$ and higher surface tension $\sigma$ give rise to an

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Fig. 6. (a) Streamline and temperature contour of plasma flow field, (b) Joule heating and radial Lorentz force contours of the plasma flow field.

Fig. 7. Particle spatial distribution on the cross section at axial distance of 12 cm: (a) number, (b) Sauter mean radius, nm (c) temperature, K, (d) velocity, m/s.
obvious increase in droplet size. The effects of liquid relaxation time $\lambda_1$, zero shear viscosity $\eta_0$ and injection pressure $P_0$ on effervescent performance are appreciably but not significantly. The liquid breakup is a process that the magnitude of the aerodynamic force exceeds the liquid surface tension and viscosity force, therefore, higher injection and smaller nozzle orifice which are benefited for enhance the aerodynamic force result in finer atomization. While the increase of rheological properties ($\lambda_1$ and $\eta_0$) makes the visco-elastic liquid more stringy to resist the disruptive force, causing drop size increasing. In order to compare the behavior of the pure solvent and visco-elastic fluid, the calculated results of pure ethanol under the same operating condition of base case has been added into Fig. 4. It shows that the non-Newtonian fluid has much higher atomized droplet size than that of pure ethanol. The increase in solid particle in suspension will dramatically increases the liquid relaxation time, which is 1.0e-4 of the base case, and deteriorating the atomization effects.

7.2. Influence on particle size, temperature and velocity

The streamline and temperature contour of plasma field in the RF torch for the base case are presented in Fig. 6(a). It shows the highest temperature of the plasma field called plasma core is a ring region located at the side of the torch axis, corresponding to the coil region. The temperature of the plasma core can reach as high as $10^4$ K, which is maintained by the Joule heating as shown in Fig. 6(b). Beside the plasma core, the temperature of the region near the axis is relatively low due to the cooling effect of the carrier gas with low temperature and large flow rate. The contours of Joule heating and Lorentz force are presented in Fig. 6(b). The Lorentz force at radial direction, $F_r$, acts toward the axial and also has two peaks for the large coil pitch-diameter ratio. It also can be seen from Fig. 6(a), due to the power input in the base case is up to 33 KW, the Lorentz force (shown in Fig. 6(b)) at radial direction is large enough to form the re-circulating flows, which will lead to a rapid decay of jet momentum and prolong the residence time of the particles entrained into the re-circulating flow.

In order to have an insight into the particle in-flight characteristics, Fig. 7 illustrates the particle spatial distribution on the cross section at axial distance of 12 cm for the base case. At axial distance of 12 cm, some of the suspension droplets are totally vaporized and the solid particles are exposed to the plasma environment. The suspension droplets and nano/agglomerate solid particles co-existed in the plasma field at that moment. Fig. 7 shows that most particles are concentrated at the spray center, having larger mean size, lower temperature and higher velocity. This is because the center of the cross section is corresponding to the spray axis region where the temperature is lower due to the cooling effect of the carrier gas. Thus the particles are difficult to get heat. On the contrary, the particles located at peripheral of the cross section are fewer, smaller, slower and more likely to overheat. This region represents the main plasma field where the plasma gas temperature is much higher than that of axis center, resulting in the melting and evaporation of particles. Furthermore, the re-circulating flows are which will give rise to slower particle velocity.

In Figs. 8 and 9, particle mean temperature, velocity and size histories are presented to study the influence of different atomization parameters and liquid rheological properties, respectively. The particle mean radius $SMR$ is averaged based on the mass average of solid and solvent size: $SMR = (1 - a_s)SMR_{sol} + a_sSMR_{sl}$ in which $a_s$ is the mass fraction of solid content in suspension. The droplet mean velocity and mean temperature are defined in a same way.

Based on the above analysis of Fig. 5, Ar-to-liquid mass flow ratio and nozzle orifice size are the most effective atomization parameters. It is noted that the changes of ALR and nozzle diameter not only influence the primary atomization, but also impact on the flow pattern. ALR of 0.12 corresponds to the carrier gas flow rate of 9 SLM as liquid mass flow rate is constant. Larger nozzle orifice is obtained by adjusting the torch dimensions of nozzle 1 diameter and wall thickness (Table 1). It can be observed from Fig. 8(a) that when particle traveling downstream, the particle mean size dramatically decreases as the solvent of suspension droplets vaporization. While when traveling further to 16 cm, the mean particle size curve will exhibit fluctuation, due to the small nano-particles are burned up. Fig. 8 also shows the case of larger nozzle size will result in lower
particle temperature and velocity. From Fig. 8 it is interesting to see that there is a self-harmonization in the adjustment of ALR and nozzle exit. For instance, higher ALR and smaller nozzle size will produce smaller particle and higher velocity. The smaller particle has lower heat capacity and needs less time to get heated, which can just compensate the loss of particle heating time for higher velocity. Therefore, the discharge period of all the cases in Fig. 8 approximately reside at the axial distance from 10 cm to 14 cm.

Fig. 9 investigates the effects of liquid and solid particle physical properties on particle velocity, size and temperature. In Fig. 9, the case of water takes the solvent as water instead of ethanol. As listed in Table 4, compared to ethanol, water has much smaller specific heat, considerable higher surface tension and latent heat of vaporization, slightly larger boiling point and comparably thermal conductivity and density. The case of solid content 7% reduced the solid particle mass content of the suspension from 15% to 7%, which alleviates the non-Newtonian behavior, resulting in smaller zero shear viscosity and relaxation time. At the beginning of the spray, Fig. 9(a) shows compared to the base case, an increase in liquid surface tension (case water) leads to larger primary atomized drop, while an reduction in solid particle content results in finer atomization performance due to smaller zero shear viscosity and relaxation time. Fig. 9(b) and (c) indicates the variation of liquid rheological properties has little influence on the flow field and initial velocity, as well as the temperature. At the downstream of the spray, Fig. 9 shows the case of water is more likely to get heat and evaporation as the specific heat of water is about 1/6 of that of ethanol, which means the efficiency of heating transfer is quite higher for water solvent. It is also can be seen from Fig. 9, although the case of solid content 7% increase the total content of liquid solvent which means it needs more energy to compensate the latent heat of liquid evaporation, the particle radius still decreasing faster than that of base case, and finally resulting in higher particle temperature and velocity. This is because the improvement of atomization effect dramatically increases the total droplet surface area and then enhances the particle heating transfer with the plasma field.

8. Conclusion

Based on the ligament formation assumption and dispersion relationships, the non-Newtonian liquid primary atomization model has been established. Two linear instability analysis for visco-elastic liquid have been compared with published experimental data. A good agreement has been achieved except for ALR smaller than 0.04. Then, the breakup model and a nano-particle model have been implemented into a radio frequency inductively coupled plasma model to study the influence of atomization operating conditions and liquid physical properties on the process of the suspension plasma spray. Results show gas-to-liquid ratio is the most important factor for visco-elastic liquid breakup. For suspension plasma spray with effervescent atomization, the adjustment of ALR and nozzle exit is self-harmonization. The decrease in fluid physical properties (surface tension, zero shear viscosity and relaxation time) is benefit for finer atomization performance and particle heating transfer with the plasma field.

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