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A reduced model for nanoparticle coating in non-equilibrium plasma

B. Rovagnati [a], A.L. Yarin [a], F. Mashayek [a,*], T. Matsoukas [b]

[a] University of Illinois at Chicago, 842 W. Taylor Street, Chicago, IL 60607, United States
[b] Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802, United States

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ABSTRACT

In this Letter, a reduced model is developed based on the full model presented earlier [Yarin et al., J. Appl. Phys. 99 (6) (2006) 064310] for the deposition of amorphous hydrogenated carbon onto particles in a methane–hydrogen plasma. The reduced model is developed based on the assumption that, under certain conditions, chemistry may be decoupled from transport. The results from the reduced model are compared to the results from the full model for particle charge and growth rate of the deposited layer. It is shown that the two models are in good agreement for submicron particles that are of interest in nanoparticle coating in low-pressure plasma reactors. The reduced model is computationally far less expensive as compared to the full model and can be implemented for simulation of a large number of nanoparticles in plasma reactors.

1. Introduction

The numerical modeling of deposition kinetics in dusty plasmas requires the simultaneous solution of the plasma equations, which determine the source terms for chemical species in the plasma, and of the transport equations to the particle surface, which determine the sink terms. When dust particle loading is small and does not affect the gas phase, one may find the plasma solution using a ‘fluid’ model [1] independently from the particles. That solution could then be used as the far-distance boundary condition for a reduced model that may be used to predict deposition kinetics with significantly lower computational cost. In the present work, we develop such reduced model and test its predictions against the full model using methane–hydrogen dusty plasma as the basis for this comparison. The ultimate goal is to implement this reduced model in conjunction with our existing global plasma reactor model [1,2] to simulate the entire process of particle coating in low-pressure plasma reactors.

2. Transport equations

Dust particles act as a source/sink of species that arrive from the bulk of the plasma to the particle surface where they may react. The concentration of species j in the vicinity of a dust particle is governed by the species mass balance equation [3],

$$\frac{\partial C_j}{\partial t} = \frac{D_j}{r^2}\frac{\partial}{\partial r}\left[r^2\left(\frac{\partial C_j}{\partial r} + \frac{C_j z_j \mu_j}{D_j}\frac{d\phi}{dr}\right)\right], \tag{1}$$

where r is the radial distance from the center of the dust particle, C_j is the local concentration of the species, z_j is the charge valence, μ_j is the electric mobility of the species, D_j is the diffusion coefficient, and ϕ is the local electric potential. For neutral species, $z_j = 0$, and the flux is entirely due to diffusion.

For charged species (ions and electrons), the diffusional flux is enhanced or retarded by the electrostatic interaction with the particle and other charged species. The electric potential is governed by the Poisson equation, which accounts for the interaction among all charges present [3],

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right) = -\frac{e}{\epsilon_0}\sum z_j C_j, \tag{2}$$

where ϵ_0 is permittivity of free space. Eqs. (1) and (2), along with suitable boundary conditions, specify the time-dependent behavior of the system and must be solved in tandem. The boundary condition at $r = \infty$ is fixed by the species concentrations in the bulk, $C_{j\infty}$, and the electroneutrality ($\phi = 0$). The inner boundary conditions require special attention when the dust particle size is smaller than the mean free path of the plasma species, as is indeed the case in low-pressure dusty plasmas. The boundary conditions are discussed separately for neutral and charged species.

Neutral species are dealt by matching the continuum and kinetic fluxes on a vacuum sphere of radius $\Delta = R_p + \lambda$, where R_p is the dust particle radius, and λ is the mean free path of the gas-phase species. This vacuum sphere divides the space into two regions, one in which continuum transport applies ($r > \Delta$) and one in which collisionless transport prevails ($r < \Delta$). The fraction of the incoming flux at Δ that is captured by the particle is $(R_p/\Delta)^2$; therefore, the net flux, Γ_{pj}, at the particle surface is [4,5]

* Corresponding author. Tel.: +1 312 996 1154.
E-mail address: mashayek@uic.edu (F. Mashayek).

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$$\Gamma_{pj} = \frac{1}{4} C_{j\Delta} \bar{v}_j F \tag{3}$$

with the view factor, F, defined as

$$F = \frac{\Delta^2}{R_p^2 + \lambda^2} \tag{4}$$

where $C_{j\Delta}$ is the species concentration at $r = \Delta$ and $\bar{v}_j = (8kT/\pi M_j)^{1/2}$ is the thermal velocity. Here, T is the temperature of the plasma; k is Boltzmann's constant and M_j is the molecular weight of species j. This equation provides the inner boundary condition at $r = \Delta$ for Eq. (1).

For charged species the situation is similar except that the fraction of the flux arriving at $r = \Delta$ that is captured by the particle is $\gamma_j (R_p/\Delta)^2$; therefore,

$$\Gamma_{pj} = \frac{1}{4} C_{j\Delta} \bar{v}_j \gamma_j F, \tag{5}$$

where $\gamma_j > 1$ for attraction and $\gamma_j < 1$ for repulsion. The factor γ_j is determined by the geometry of ion and electron trajectories between the surface of the vacuum sphere and the particle. In the general case [4] it depends on the radius of the vacuum sphere but if this is sufficiently large, such that the electrostatic interaction between particle and charged species at $r = \Delta$ is small, the result reduces to the classical expression from the orbit-motion limit (OML) calculation, which yields the factor γ_j as [6,7]

$$\gamma_j = \begin{cases} 1 - \frac{z_j e Q_p}{4\pi \epsilon_0 k T_j R_p} & \text{for } z_j Q_p < 0; \\ 1 & \text{for } z_j Q_p = 0; \\ \exp\left(-\frac{z_j e Q_p}{4\pi \epsilon_0 k T_j R_p}\right) & \text{for } z_j Q_p > 0, \end{cases} \tag{6}$$

where Q_p is the particle charge, and T_j is the species temperature.

The inner boundary condition for the Poisson equation is applied at $r = \Delta$,

$$\phi|_\Delta = \frac{Q_p + (\sum_j z_j e C_{j\Delta}) V_\Delta}{4\pi \epsilon_0 \Delta}. \tag{7}$$

The numerator in this expression is the net charge inside the vacuum sphere and consists of the charge on the particle, Q_p, plus the charge due to all ions and electrons inside the volume V_Δ of the vacuum sphere. This expression assumes the concentration of ions and electrons in the vacuum sphere to be uniform and equal to their value at the surface, an approximation that is acceptable if the Debye length is large. Finally, the radius of the vacuum sphere is calculated according to Fuchs as [4]

$$\frac{\Delta}{R_p} = \frac{1}{Kn^2}\left[\frac{2}{15}\left(Kn^2+1\right)^{5/2} + \frac{(Kn+1)^5}{5} - \frac{1}{3}\left(Kn^2+1\right)(Kn+1)^3\right], \tag{8}$$

where $Kn = \lambda/R_p$ is the particle Knudsen number. For $Kn > 10$ the above expression reduces to $\Delta/R_p \approx Kn$. In this limit, the last gas-phase collision before a species could be captured at the particle surface occurs at a distance of one mean free path.

3. The reduced model

The above set of equations constitute a closed system that describes the evolution of the plasma species in the space surrounding the dust particle. The calculation produces concentration profiles of all species, and their overall flux to the particle surface. The particle charge is obtained from the flux of all charged species at $r = \Delta$. Similarly, the deposition rate is obtained by summing the flux of all species that deposit mass on the particle. The computational cost for this hybrid model is substantial, especially considering that a simple reactive plasma such as methane requires 20 species that participate in more than 30 chemical reactions [3]. Significant computational savings can be realized by taking advantage of the large difference between the size of the dust particles compared to all other length scales in the problem. If the size of the vacuum sphere is much larger than the particle size, concentration and charge gradients outside this sphere make negligible contributions to the fluxes on the particle surface. In this case, the far-distance species concentrations may be obtained separately and used as input for the calculation of fluxes at the particle surface by kinetic expressions entirely. To assess the validity of this approach, we compare the reduced form of the kinetic model to the full hybrid form for the case of a reactive methane dusty plasma. The full hybrid model for this system was described previously [3] and was shown to provide good agreement with experimental measurements of deposition rates in hydrocarbon plasmas [8–11].

The system that forms the basis for studying the range of validity of the reduced model is a hydrogen–methane dusty plasma. The plasma is assumed at steady-state with the gas temperature $T = 500$ K and the electrons temperature $T_e = 1$ eV. Hydrogen and methane species are continuously supplied to keep their concentrations constant at the far-end boundary. The gas–gas reaction mechanism comprises of electron–neutral, ion–neutral, and neutral–neutral reactions. These sustained a reactive pool with a total of 20 species, namely, H, H_2, H_2^+, H_3^+, CH, CH_2, CH_3, CH_3^+, CH_4, CH_4^+, CH_5^+, C_2H_2, $C_2H_2^+$, C_2H_4, $C_2H_4^+$, C_2H_5, $C_2H_5^+$, C_2H_6, C_3H_8 and e^-. At the particle surface, direct deposition of CH_2, CH_3, C_2H_5, and associated ions is modeled by implementing a sticking model. Etching, discharge and dissociation, pure discharge, and discharge and etching are also considered. The reactive plasma is characterized by a mean free path, λ, of approximately 0.5 mm, and ion Debye length, Λ_D, equal to 0.05 mm. Charging and coating of particles with size range between 10 nm and 1000 nm are considered.

In our previous work [3], the solution of the above plasma system was obtained for the full model where the species equations were solved outside the vacuum sphere. In the present work, the results are obtained for the same system using the reduced model where the steady-state flux of neutral and charged species is obtained from Eqs. (3) and (5), respectively. In the reduced model, the species equations outside the vacuum sphere are not integrated; instead the species concentrations at the surface of the vacuum sphere are assumed to be the same as the concentrations obtained from the solution of the fluid model for the plasma without the effect of the particles. As a result, the reduced model offers a substantially more efficient computational procedure.

Since the flux of charged species is dependent on the particle charge, which in return depends on the flux of charged species, the quasi-steady state particle charge must be determined first. This is obtained by imposing a current balance of the charged species at the particle surface,

$$\left(\frac{T_e}{M_e}\right)^{1/2} \exp\left(-\frac{z_j e Q_p}{4\pi \epsilon_0 k T_j R_p}\right) C_{\Delta,e} = \left(1 - \frac{z_j e Q_p}{4\pi \epsilon_0 \pi k T_j R_p}\right) \sum_{i=ions} \left(\frac{T_i}{M_i}\right)^{1/2} C_{\Delta,i}, \tag{9}$$

which is solved for Q_p. This equation is obtained by equating the positive and negative fluxes to the particle.

Knowledge of fluxes of sticking radicals and of ions contributing to the particle allows prediction of the film growth rate [3],

$$\frac{dh}{dt} = \frac{\Gamma_C}{N_A d} 12(1 + H/C), \tag{10}$$