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Transient Nano-Dense Molecular States as a Persistence–Stabilization Closure for Combustion Nanoparticle Inception

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Abstract

Nanoparticle inception remains one of the least constrained steps in predictive combustion particle modeling. In soot models, detailed gas-phase chemistry can describe fuel decomposition, aromatic growth, PAH chemistry, radical pathways, oxidation, surface growth, and coagulation, yet the conversion of molecular precursors into the first persistent particles is often represented by empirical nucleation rates, selected dimerization reactions, or source terms into a first particle bin. Similar uncertainty occurs in inorganic flame-aerosol models, where the earliest molecular-to-particle transition is frequently reduced to classical or semi-empirical nucleation expressions. This paper formulates the transient nano-dense molecular state (NDMS) hypothesis as a practical persistence–stabilization closure for this inception gap. NDMS is defined as a transient, non-equilibrium, locally dense ensemble of associated molecular or sub-molecular precursor units that remains reversible on the dissociation timescale and contributes to particle inception only when chemical or structural stabilization competes successfully with dissociation and other losses. The framework separates precursor association, cluster dissociation, competing non-stabilizing loss, and stabilization into distinct model components. It introduces an operational density-enhancement criterion, association- and stabilization-weighted precursor descriptors, bounded stabilization probabilities, and a minimal zero-dimensional demonstration. Implementation routes are outlined for detailed chemistry, sectional population balances, moment methods, and reduced CFD closures. For soot, the framework provides a structured way to couple PAH clustering with radical-driven stabilization and chemical aging. For inorganic systems, illustrated using TiO_2 formation, NDMS is treated cautiously as a system-specific modeling architecture for reactive oxide-cluster formation rather than as evidence of a universal microscopic pathway. The hypothesis is presented as falsifiable: it should be retained only where constrained NDMS closures improve inception-specific observables such as onset location, pressure dependence, early particle number density, precursor sensitivity, and cluster-sensitive diagnostics.

Keywords: nanoparticle inception; soot; flame aerosol synthesis; transient nano-dense molecular state; persistence-stabilization; PAH clustering; detailed chemistry; population balance; inorganic nanoparticles; nucleation closure

1. Introduction and purpose

Nanoparticle formation in combustion is central to both pollutant formation and materials synthesis. In hydrocarbon flames, soot affects radiation, flame structure, engine performance, health-relevant emissions, and climate forcing. In flame aerosol synthesis, related high-temperature gas-to-particle pathways are used to produce inorganic nanoparticles such as titania, silica, alumina, zirconia, and mixed oxides [19-23,38-41]. Although the final materials differ, both classes of systems contain a difficult modeling transition: reactive molecular precursors must become the first persistent particles.

For carbonaceous particles, detailed mechanisms describe fuel pyrolysis, formation of small radicals and unsaturated species, first aromatic-ring formation, PAH growth, radical chemistry, and oxidation

with increasing sophistication [1-6]. These mechanisms are indispensable because they connect fuel structure, temperature, equivalence ratio, residence time, and radical pools to precursor formation. However, even a highly detailed gas-phase mechanism still requires an inception rule. Many models therefore convert selected molecular species, often one or a few PAHs, into particles through empirical nucleation rates, dimerization steps, or source terms into a first particle bin [4-6,29-37].

This simplification is computationally useful, but it compresses several different physical and chemical events into one closure. Molecular simulations and flame experiments show that PAH association can be reversible at flame temperatures and that physical clustering alone may not always create persistent soot precursors [7-10]. At the same time, radical chemistry, covalent linking, hydrogen loss, aromatization, and chemical aging can stabilize transient aromatic assemblies [11-15]. High-resolution structural studies of incipient soot further indicate that early soot material is chemically complex, structurally heterogeneous, and not adequately represented by a single precursor molecule or by purely equilibrium condensation [16-18].

An analogous uncertainty appears in inorganic flame aerosol synthesis. Models frequently include precursor decomposition, oxidation or hydrolysis, homogeneous nucleation, condensation, coagulation, aggregation, sintering, and crystallization [19-23,38-41]. These models are powerful for predicting particle size and morphology after stable particles appear. The earliest molecular-to-particle conversion, however, is often described by classical nucleation theory or fitted cluster-source terms. Such approaches may be adequate in some regimes, but they can be limited when small reactive clusters do not behave as equilibrium droplets with macroscopic surface properties [24-27].

The purpose of this paper is to establish the transient nano-dense molecular state (NDMS) as an appropriate modeling hypothesis for this inception gap [28]. The hypothesis is not that soot and inorganic particles form by the same chemistry. They indeed do not. The hypothesis is that some combustion nanoparticle-inception processes can be modeled more objectively as a competition between reversible local clustering and irreversible or semi-irreversible stabilization than as an instantaneous molecular-to-particle jump. The contribution is therefore a modeling architecture: association creates transient locally dense clusters, dissociation removes unstable clusters, and stabilization converts a fraction of them into persistent particle precursors.

The paper is written as an applied framework rather than as proof of a new physical phase. It defines the minimum NDMS claim, formulates the core source terms, explains implementation routes, identifies the advantages over direct empirical nucleation, and states how the hypothesis can be tested or weakened by data. This positioning is essential: NDMS should be accepted or rejected as a useful, constrained, falsifiable inception closure, not as an unconstrained name for every pre-particle cluster.

The novelty of the present framework is not the isolated recognition of clustering, radical stabilization, or subcritical cluster populations, each of which has precedent in the literature. Rather, the contribution is to combine these elements into a single inception closure in which association, dissociation/loss, and stabilization are explicitly separated, weighted by distinct precursor descriptors, and linked to bounded persistence–stabilization probabilities suitable for detailed chemistry, population-balance, moment, and reduced CFD implementations.

2. Existing modeling approaches and the inception gap

2.1 Detailed soot chemistry

Detailed soot mechanisms provide the strongest available description of molecular precursor formation. They include fuel-fragment chemistry, radical pools, first aromatic-ring formation through propargyl recombination and other routes, PAH growth through H-abstraction-C_2H_2-addition (HACA), phenyl

addition and cyclization, radical recombination, and related pathways [1-6]. Their strength is chemical interpretability: they identify which molecular families are present near particle onset and how flame conditions change precursor production.

Their limitation is that chemistry alone does not define persistence. A mechanism can predict pyrene, coronene, indenyl-type radicals, radical PAHs, oxygenated aromatics, or high-mass intermediates, but it still needs a rule that decides when these species become particles. When this rule is a single PAH dimerization step or an empirical nucleation coefficient, the most sensitive stage of the model remains weakly constrained.

2.2 PAH clustering and reversible association

Physical clustering models directly address the pre-particle state. Quantum-chemical and molecular-dynamics studies show that PAH clustering depends strongly on molecular size, compactness, temperature, interaction energy, entropy penalty, and cluster structure [7-10]. These studies support the idea that precursor association is not automatically equivalent to particle inception. At high temperature, clusters may form but dissociate before stabilizing. Therefore, reversible association is necessary to describe the pre-inception region, but it is not sufficient by itself.

2.3 Radical-driven stabilization

Recent soot literature has emphasized resonance-stabilized radicals and radical-driven pathways as important for inception and early growth [11-15]. Radical chemistry offers a route by which transient molecular encounters become chemically persistent through recombination, covalent linking, continued mass growth, hydrogen loss, and aromatization. This evidence supports an inception view in which physical clustering increases local encounter probability while chemistry determines whether an associated cluster survives. A model that treats only physical association may miss stabilization, whereas a radical-only model may not explicitly represent local densification and repeated molecular encounters.

2.4 Population balances, moment methods, and CFD closures

Population balance models connect molecular source terms to measurable particle properties such as number density, mass, surface area, size distribution, aggregate morphology, and soot volume fraction [29-34]. Sectional and stochastic methods can represent detailed distributions, whereas moment methods such as MOMIC, QMOM, DQMOM, and HMOM reduce computational cost for multidimensional simulations [30-34]. Reduced soot models used in engineering CFD often solve for soot mass and number density with semi-empirical rates for nucleation, surface growth, coagulation, and oxidation [35-37]. In all of these methods, predictive quality depends strongly on the physical meaning of the inception source term.

2.5 Inorganic flame aerosol models

Inorganic flame-aerosol models include precursor evaporation or decomposition, oxidation, hydrolysis, homogeneous nucleation, condensation, coagulation, aggregation, coalescence, sintering, and phase transformation [19-23,38-41]. Their aerosol-dynamics foundation is strong, but the earliest stable cluster source is often based on classical nucleation or fitted expressions. Non-classical nucleation concepts, prenucleation clusters, subcritical cluster populations, and delayed structural stabilization show that molecular-to-particle transitions may require more than equilibrium droplet assumptions in some systems [24-27].

2.6 The common modeling gap

The common gap is not absence of chemistry or particle dynamics. The gap is the closure that connects them. Existing models often treat inception as a discrete and irreversible event, use a single nucleating species, weakly couple physical clustering and chemical stabilization, and represent pressure or concentration effects through calibrated coefficients rather than identifiable molecular processes. NDMS is proposed to address exactly this interface. This gap is especially important in pressure-dependent and near-threshold sooting regimes, where particle onset and early particle growth can be highly sensitive to pressure, burner configuration, lateral transport, and local thermochemical conditions [42-44].

To clarify the intended contribution of the NDMS closure, Table 1 summarizes how the proposed framework differs from several existing descriptions of nanoparticle inception. The comparison is not meant to replace these approaches. Rather, it identifies the specific modeling role of NDMS: to separate reversible precursor association from persistence-generating stabilization and to provide a structured source term for the first persistent particle population.

Table 1. Distinction between existing inception descriptions and the proposed NDMS persistence–stabilization closure.

Existing description	Captured process	NDMS addition
Direct empirical nucleation	Fitted source term based on precursor, temperature, or pressure	Separates association, dissociation/loss, and stabilization
PAH dimerization or clustering	Molecular association and reversible clustering	Treats clusters as a transient reservoir; only stabilization creates persistent particles
Radical-driven inception	Chemical stabilization by radical pathways	Couples radical chemistry to a locally dense reversible reservoir
Prenucleation/non-classical nucleation	Subcritical clusters and non-classical transitions	Adapts subcritical clustering to combustion with dissociation, oxidation/loss, and stabilization
Population-balance/moment models	Evolution after particles are introduced	Supplies a structured first-particle source term

3. Definition and minimum claim of the NDMS hypothesis

In this paper, NDMS denotes a non-equilibrium, transient, locally dense ensemble of associated molecular or sub-molecular precursor units that remains reversible on the timescale of cluster dissociation and becomes relevant to nanoparticle inception only when chemical or structural stabilization converts a fraction of the ensemble into persistent particle precursors.

The term “nano-dense” is therefore used as a scale-local modeling descriptor for enhanced precursor encounter density, not as a thermodynamic phase label. An NDMS-like region may be considered present when the effective precursor number density inside the transient associated ensemble, $\rho_{P,NDMS}$, exceeds the surrounding gas-phase precursor number density, $\rho_{P,gas}$, by a finite enhancement factor:

$$\chi_\rho = \frac{\rho_{P,NDMS}}{\rho_{P,gas}} > \chi_{\rho,crit} \qquad (1)$$

while remaining below bulk condensed-phase density. The parameter χ_ρ is therefore an operational local-density enhancement, not evidence of a distinct condensed phase. It measures whether precursor units experience a local encounter environment denser than the surrounding gas-phase precursor pool. The threshold value of χ_ρ is not assumed universal and should be determined or constrained for each system by simulation, diagnostics, or model calibration.

In practice, the condition $\chi_\rho > 1$ should be interpreted only as a minimum local-density requirement. An NDMS-relevant reservoir should also possess a finite residence time relative to the local collision, dissociation, loss, or stabilization timescales. Therefore, practical implementations may use a calibrated threshold $\chi_{\rho,crit} > 1$, a minimum lifetime criterion, or a combined density–persistence criterion. This prevents isolated short-lived collision complexes from being counted as NDMS reservoirs unless they create a locally enhanced precursor environment with sufficient persistence to participate in stabilization.

This definition contains four restrictions. First, NDMS is transient: cluster existence alone is not particle inception. Second, it is locally dense: association creates enhanced local precursor concentration and repeated encounters. Third, it is reversible: clusters can dissociate, evaporate, fragment, or return to the precursor pool. Fourth, it is conditional: persistent particles appear only if stabilization competes successfully with dissociation and other non-stabilizing losses.

The basis is intentionally chemistry-neutral at the architectural level. In soot, stabilization may involve PAH association, resonance-stabilized radicals, covalent linking, hydrogen loss, aromatization, carbonization, and chemical aging [7-18]. In inorganic systems, stabilization may involve precursor decomposition, oxidation-state evolution, ligand removal, hydrolysis, oxygen incorporation, condensation, structural rearrangement, and crystallization [19-27,38-41]. The common element is not chemical identity but kinetic structure: reversible cluster formation competes with dissociation, and stabilization creates the first persistent particle population.

4. Mathematical formulation

4.1 Association- and stabilization-weighted precursor descriptors

Instead of selecting a single nucleating molecule, the precursor pool is represented by two related but distinct weighted descriptors:

$$C_P^{assoc} = \sum_i w_i^{assoc} C_i \qquad (2a)$$

$$C_P^{stab} = \sum_i w_i^{stab} C_i \qquad (2b)$$

where C_i is the concentration of precursor class i, C_P^{assoc} is the association-weighted precursor descriptor controlling the formation of the reversible NDMS reservoir, and C_P^{stab} is the stabilization-weighted precursor descriptor controlling the chemical or structural conversion of transient NDMS clusters into persistent incipient particles. The weights w_i^{assoc} and w_i^{stab} are dimensionless factors that represent, respectively, the relative ability of precursor class i to participate in local densification and in stabilization.

With this distinction, the formation rate of the transient NDMS reservoir may be written in reduced form as

$$R_{form} = k^{on}(C_P^{assoc})^m \qquad (3)$$

where k^{on} is an effective association coefficient and m is an apparent precursor-pool order. The stabilization coefficient is then expressed as a function of the stabilization-weighted precursor descriptor and the local thermochemical environment:

$$k^{stab} = k^{stab}\left(T, C_P^{stab}, [R^{\cdot}], [H], [O_2], [OH], \dots\right) \qquad (4)$$

where $[R^{\cdot}]$, $[H]$, $[O_2]$, and $[OH]$ represent radical, hydrogen-atom, oxidizer, and reactive-species fields relevant to the specific system. This formulation separates precursor availability for association from precursor or radical availability for stabilization.

Here and below, k^{stab} should be interpreted as an effective pseudo-first-order stabilization coefficient with respect to the transient NDMS reservoir. Its local value may depend on *T*, C_P^{stab}, radical concentrations, oxidizer concentrations, H-atom availability, and other system-specific reactive fields, as indicated in Eq. (4). Once these dependencies are evaluated or parameterized for the local thermochemical state, the stabilization flux is first order in the transient reservoir concentration, $R_{stab} = k^{stab} Z$, or $R_{stab,n} = k_n^{\mathrm{stab}} Z_n$ for cluster class *n*.

For soot, C_P^{assoc} may include compact PAHs, peri-condensed PAHs, high-mass aromatic species, and other species with strong dispersion or π-stacking interactions. In contrast, C_P^{stab} may place greater weight on radical PAHs, resonance-stabilized radicals, partially saturated aromatics, covalently linked intermediates, and species capable of hydrogen loss, radical recombination, cross-linking, aromatization, or chemical aging. For inorganic systems, C_P^{assoc} may include metal-containing fragments, oxide or suboxide species, hydroxylated intermediates, ligand-bearing fragments, and small molecular clusters, whereas C_P^{stab} may emphasize species or pathways involved in oxidation, hydrolysis, ligand removal, oxygen incorporation, network formation, structural rearrangement, or crystallization.

The weights should be chosen according to model resolution. In the simplest implementation, binary inclusion weights may be used, with $w_i^{assoc} = 1$ or $w_i^{stab} = 1$ for included precursor classes and zero for excluded classes. A more mechanistic implementation can use property-based weights derived from molecular size, aromatic ring number, compactness, polarizability, radical character, binding energy, oxidation state, ligand content, or calculated stabilization tendency. In reduced calibrated models, the weights should be constrained by inception-specific observables such as onset location, early particle number density, pressure dependence, precursor sensitivity, or cluster-sensitive diagnostics. This hierarchy is important because it prevents the precursor descriptors from becoming unconstrained fitting expressions.

This distinction also clarifies the physical structure of the closure. C_P^{assoc} controls the birth of the reversible NDMS reservoir, Z or Z_n. The reservoir population then competes between dissociation, other losses, and stabilization. Only the stabilization flux contributes to the persistent incipient particle source. Thus, precursor-pool concentration, transient NDMS reservoir concentration, and persistence-stabilized particle formation remain separate model quantities.

4.2 Reversible cluster formation and stabilization

A representative transient cluster Z_n contains *n* precursor units or an equivalent precursor mass. The essential kinetic structure is:

$$C_P^{assoc} + Z_n \rightleftharpoons Z_{n+1} \qquad (5)$$

$$Z_n \rightarrow P_n \qquad (6)$$

where P_n denotes a stabilized incipient particle precursor. Association and dissociation define the reversible NDMS reservoir, while stabilization transfers part of that reservoir into the persistent particle population. The corresponding cluster balance can be written schematically as:

$$\frac{dZ}{dt} = \text{formation by association - loss by dissociation} - \text{loss by non-stabilizing processes - loss by stabilization} \qquad (7)$$

For a minimal one-reservoir model, this becomes

$$\frac{dZ}{dt} = R_{form} - R_{diss} - R_{loss} - R_{stab}$$

then:

$$\frac{dZ}{dt} = k^{on}(C_P^{assoc})^m - k^{off}Z - k^{loss}Z - k^{stab}Z \qquad (8)$$

where k^{on} is an effective association coefficient, k^{off} is an effective dissociation coefficient, k^{loss} is an effective non-stabilizing loss coefficient, k^{stab} is an effective chemical or structural stabilization coefficient, and m is an apparent precursor-pool order. Nevertheless, in the one-reservoir reduction, $k^{on}(C_P^{assoc})^m$ should be interpreted as the net birth rate of the unresolved NDMS reservoir, not as the elementary growth step of Eq. (5).

Depending on whether *Z* is expressed as a mass or number concentration, the particle source may be written as:

$$S_{mass}^{NDMS} = k^{stab}Z^{mass} \quad or \quad S_{num}^{NDMS} = k^{stab}Z^{num} \qquad (9)$$

Here Z^{mass} denotes the NDMS reservoir expressed as mass concentration, whereas Z^{num} denotes the NDMS reservoir expressed as number concentration.

4.3 Persistence-stabilization criterion

The competition between cluster loss and stabilization can be expressed through a persistence–stabilization (PS) number:

$$Da_{\mathrm{PS},n} = \frac{k_n^{\mathrm{stab}}}{k_n^{\mathrm{off}} + k_n^{\mathrm{loss}}} \qquad (10)$$

where k_n^{stab}, k_n^{off}, and k_n^{loss} are first-order stabilization, dissociation, and competing-loss rate coefficients for cluster class n, respectively. The term k_n^{loss} represents non-stabilizing removal processes such as oxidation, fragmentation, dilution, or transport out of the inception region.

When

$$k_n^{\text{stab}} \ll k_n^{\text{off}} + k_n^{\text{loss}}$$

or equivalently

$$Da_{PS,n} \ll 1$$

stabilization is too slow to compete with cluster removal, and most NDMS clusters remain transient or are lost before contributing to persistent particle formation. When

$$k_n^{\text{stab}} \gtrsim k_n^{\text{off}} + k_n^{\text{loss}}$$

or equivalently

$$Da_{PS,n} \gtrsim 1$$

stabilization competes effectively with dissociation and other loss processes, and particle inception becomes more likely.

The corresponding bounded stabilization probability is:

$$P_{\text{stab},n} = \frac{k_n^{\text{stab}}}{k_n^{\text{off}} + k_n^{\text{stab}} + k_n^{\text{loss}}} = \frac{Da_{\text{PS},n}}{1 + Da_{\text{PS},n}} \qquad (11)$$

The resulting NDMS closure can be interpreted as a three-level modeling structure linking gas-phase chemistry to persistent particle formation. The first level defines association- and stabilization-weighted precursor descriptors, C_P^{assoc} and C_P^{stab}. The second level is the reversible transient NDMS reservoir, Z_n, characterized by local precursor-density enhancement and finite residence time. The third level is the persistence-stabilized incipient particle source.

Figure 1 summarizes these levels and the main transition criteria between them: local association and densification for formation of the NDMS reservoir, and persistence–stabilization, expressed through $Da_{PS,n}$ or $P_{stab,n}$, for transfer into the persistent particle population.

4.4 Effective association free energy

Reversible cluster persistence can be parameterized through an effective association free energy. A compact expression is:

$$\Delta G_n^{assoc} = \Delta G_n^o - \nu_n RT \ln a_P^{assoc} \qquad (12)$$

where ΔG_n^o is the standard-state free-energy contribution associated with forming cluster class n, a_P^{assoc} is the effective activity or supersaturation associated with the association-weighted precursor descriptor, and ν_n is the effective number of precursor units involved in the lumped association event. The value of ν_n depends on how the cluster process is represented: ν_n = 1 for monomer addition to an existing cluster, $Z_n + C_P^{assoc} \rightarrow Z_{n+1}$, whereas $\nu_n = n$ may be used for direct lumped formation of an n-unit cluster from precursor units. The standard term may be decomposed as:

$$\Delta G_n^o = \Delta H_n^{int} + T\Delta S_n^{loss} + \Delta G_n^{pack} \qquad (13)$$

where ΔH_n^{int} represents net intermolecular interaction enthalpy, $\Delta S_n^{loss} > 0$ denotes the magnitude of translational, rotational, and configurational entropy lost during association, and ΔG_n^{pack} represents packing, structural, or configurational penalties. Favorable association corresponds to more negative ΔG_n^{assoc}. This formulation is not intended to prove an equilibrium condensed phase; it only provides a thermodynamic parameterization of whether local conditions can support a transient cluster population with finite residence time.

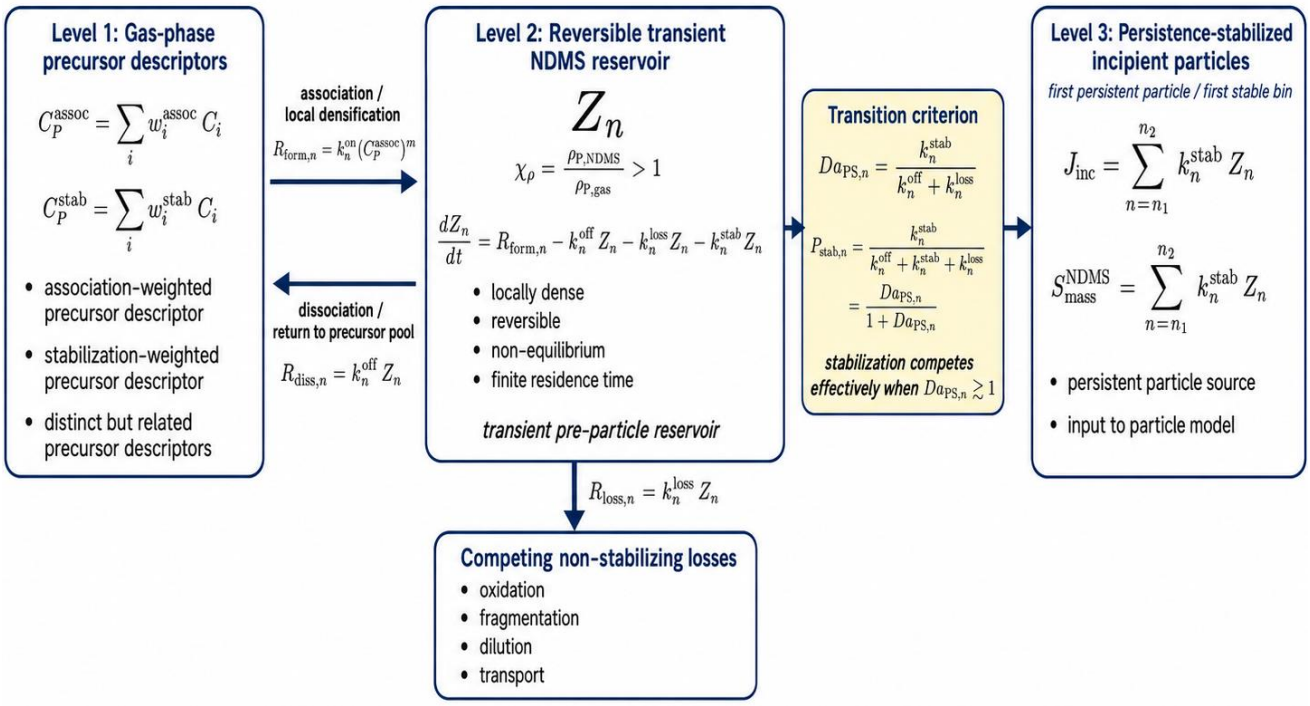

Figure 1. Three-level mathematical structure of the NDMS persistence–stabilization closure for nanoparticle inception. The closure separates gas-phase precursor descriptors, the reversible transient NDMS reservoir, and persistence-stabilized incipient particles. Formation of Z_n is controlled by association through C_P^{assoc}, local density enhancement $\chi_\rho > 1$, and finite residence time, while transfer to the persistent particle population is controlled by $Da_{PS,n}$ and $P_{stab,n}$ in competition with dissociation and non-stabilizing losses.

4.5 Minimal zero-dimensional demonstration

A conventional reduced inception model may write:

$$J_{\mathrm{dir}} = k_{\mathrm{nuc}} C_P^m \qquad (14)$$

where k_{nuc} compresses association, dissociation, stabilization, pressure effects, and chemical environment into one coefficient.

For the minimal zero-dimensional demonstration, Eq. (8) is evaluated under quasi-steady conditions. The association-weighted precursor descriptor C_P^{assoc} is treated as locally constant over the NDMS adjustment timescale, stabilization and loss processes are assumed first order in Z_n, and $dZ_n/dt \approx 0$.

$$Z_n = \frac{k_n^{\mathrm{on}}(C_P^{assoc})^m}{k_n^{\mathrm{off}} + k_n^{\mathrm{loss}} + k_n^{\mathrm{stab}}} \qquad (15)$$

and therefore

$$S_{NDMS,n} = k_{\mathrm{n}}^{stab} Z_n = \frac{k_{\mathrm{n}}^{stab} k_{\mathrm{n}}^{on} (C_P^{assoc})^m}{k_{\mathrm{n}}^{off} + k_n^{\mathrm{loss}} + k_{\mathrm{n}}^{stab}} \qquad (16)$$

Expression (16) shows the minimum new behavior introduced by the NDMS closure. Particle inception depends not only on precursor availability through C_P^{assoc}, but also on whether transient clusters survive dissociation and other losses long enough to stabilize.

If Z_n is treated as a mass concentration of transient NDMS clusters, the stabilization flux into persistent particles is written as:

$$S_{mass}^{NDMS} = k^{stab} Z$$

where S_{mass}^{NDMS} has units of mass per volume per time. If a particle-number source is required, it can be obtained as:

$$J_{num}^{NDMS} = \frac{S_{mass}^{NDMS}}{m_{inc}}$$

where m_{inc} is the representative mass assigned to the first persistent particle or first particle bin.

To illustrate the effect of the persistence–stabilization competition in the reduced zero-dimensional closure, Table 2 reports representative dimensionless cases for a fixed reservoir formation rate, $k_n^{\mathrm{on}} (C_P^{assoc})^m = 1$. The values are not fitted parameters and are used only to show how dissociation, non-stabilizing losses, and stabilization jointly determine $P_{stab,n}$ and the resulting NDMS inception source.

Table 2. Illustrative three-channel persistence–stabilization behavior for $k_n^{\mathrm{on}} (C_P^{assoc})^m = 1$. Values are dimensionless demonstration values, not fitted parameters.

Case	k_n^{off}	k_n^{loss}	k_n^{stab}	P_n^{stab}	J_{NDMS} for $k_n^{\mathrm{on}} (C_P^{assoc})^m = 1$
Rapid removal	10	1	0.1	0.009	0.009
Comparable loss and stabilization	0.7	0.3	1	0.50	0.50
Strong stabilization	0.05	0.05	10	0.990	0.990

The numerical values are arbitrary and are not presented as validation. The purpose of this demonstration is not quantitative prediction, but to show that two systems with the same precursor association rate can yield very different inception sources when dissociation, loss, and stabilization compete.

5. Implementation hierarchy

5.1 Detailed chemistry coupled to cluster master equations

The most scientifically direct implementation is to couple detailed gas-phase chemistry with a cluster master equation. The detailed mechanism solves:

$$\frac{dC_i}{dt} = \dot{\omega}_i(T, C) \qquad (17)$$

for fuel fragments, aromatics, PAHs, radicals, oxidizers, and products. The NDMS extension introduces cluster populations Z_n:

$$\frac{dZ_n}{dt} = \beta_{n-1} C_P^{assoc} Z_{n-1} - \beta_n C_P^{assoc} Z_n + \alpha_{n+1} Z_{n+1} - \alpha_n Z_n - k_n^{stab} Z_n - k_n^{loss} Z_n \qquad (18)$$

Here β_n is the association coefficient, α_n the dissociation coefficient, k_n^{stab} is the stabilization coefficient, and k_n^{loss} is the competing non-stabilizing loss coefficient. The resolved NDMS domain is taken as $n_1 \leq n \leq n_2$, where n_1 is the smallest cluster class treated as part of the transient NDMS reservoir and n_2 is the largest reversible cluster class before transfer to the persistent particle phase.

The incipient-particle source is:

$$J_{inc} = \sum_{n=n_1}^{n_2} k_n^{stab} Z_n \qquad (19)$$

The units of J_{inc} depend on the definition of Z_n. If Z_n is a number concentration, J_{inc} is a number source. If Z_n is a mass concentration, the same expression represents a mass-transfer source into the persistent particle phase.

The cluster classes Z_n do not need to represent individual molecular isomers. They may be lumped by size, aromaticity, radical content, oxygen content, metal content, oxide composition, or compactness. This implementation preserves detailed chemistry while avoiding the assumption that every precursor collision creates a particle.

For soot, k_n^{stab} may represent radical recombination, covalent bridge formation, hydrogen loss, aromatization, ring condensation, carbonization, or chemical aging. A general closure is:

$$k_n^{stab} = A_n T^{b_n} \exp\left(-\frac{E_{a,n}}{RT}\right) F_{rad} F_H F_{comp}(n) \qquad (20)$$

where F_{rad} accounts for the local abundance of resonance-stabilized radicals or other reactive radicals, F_H accounts for H-abstraction or H-atom availability, and $F_{comp}(n)$ accounts for cluster compactness or internal restructuring. For inorganic systems, k_n^{stab} may represent oxidation, hydrolysis, ligand removal, oxygen incorporation, Ti-O-Ti or Si-O-Si network formation, structural reorganization, crystallization onset, or conversion to a persistent amorphous oxide cluster.

The needed parameters can be estimated from quantum chemistry, molecular dynamics, statistical mechanics, and experiments. Binding energies and dimerization equilibria can inform k_n^{off}. Collision

theory and sticking probabilities can inform k_n^{on}. Radical recombination or structural transformation kinetics can inform k_n^{stab}. Experimental particle onset, pressure dependence, and early size distributions can constrain the combined model.

5.2 Sectional population balances

In a sectional population balance, NDMS can be introduced as one or more reversible pre-particle sections between gas-phase precursors and stable particles. These sections have finite association, dissociation, and stabilization fluxes. Their effective density or compactness should not be treated as an arbitrary constant; it should be constrained by molecular structure, temperature, cluster size, and composition. The advantage is that the model no longer jumps directly from gas-phase species to a solid first bin. It contains a reversible and chemically active pre-particle population.

5.3 Moment closures

For moment methods and CFD, resolving a full cluster distribution may be too expensive. A reduced implementation can therefore use one transported scalar Z representing the mass concentration of transient NDMS clusters. In this formulation, the association-weighted precursor descriptor C_P^{assoc} supplies the transient cluster reservoir, while Z is depleted by dissociation, competing non-stabilizing losses, and stabilization into persistent particles:

$$\frac{dZ}{dt} = R_{form} - R_{diss} - R_{loss} - R_{stab} \qquad (21)$$

with rate definitions:

$$R_{form} = k^{on}(C_P^{assoc})^m$$
$$R_{diss} = k^{off} Z$$
$$R_{loss} = k^{loss} Z$$
$$R_{stab} = k^{stab} Z$$

Here, R_{form} represents the net local formation rate of the transient NDMS reservoir through precursor association, R_{diss} represents return of transient clusters to the precursor pool, R_{loss} represents competing non-stabilizing removal processes such as oxidation, fragmentation, dilution, or transport out of the inception region, and R_{stab} represents conversion of the transient NDMS reservoir into persistence-stabilized incipient particles.

In this reduced moment or CFD form, Z is interpreted as a **mass concentration**. Therefore, R_{stab} is a **mass source** into the persistent particle phase. If a particle-number source is required, it may be obtained by dividing the mass source by an assumed representative incipient-particle mass or first-bin mass.

5.4 Reduced CFD closures

For engineering CFD, NDMS should be introduced with the smallest possible number of additional empirical parameters. A conventional nucleation expression can be modified as:

$$J_{red} = J_{base} F_{NDMS} \qquad (22)$$

where F_{NDMS} is a bounded persistence-stabilization factor. A physically safer form is:

$$F_{\mathrm{NDMS,n}} = \left[\frac{Z_n}{Z_n + Z_n^*}\right] P_{stab,n} = \left[\frac{Z_n}{Z_n + Z_n^*}\right]\left[\frac{k_n^{\mathrm{stab}}}{k_n^{\mathrm{off}} + k_n^{\mathrm{stab}} + k_n^{\mathrm{loss}}}\right] \qquad (23)$$

The first factor represents finite transient-cluster population, while the second factor represents stabilization probability. Because both factors are bounded, the correction does not become an uncontrolled multiplier. Temperature, pressure, radical concentration, oxidizer concentration, and precursor composition should enter through k_n^{on}, k_n^{off}, k_n^{stab}, k_n^{loss}, and Z_n rather than through independent empirical exponential factors. This is particularly relevant for high-pressure and near-threshold premixed flames, where pressure and lateral transport can strongly influence the apparent onset and spatial development of soot formation [42-44].

6. Carbonaceous and inorganic applications

6.1 Carbonaceous particles

For soot, NDMS should be modeled as a reactive aromatic-cluster ensemble. The precursor pool should include not only stable PAHs but also radical intermediates and partially saturated or linked aromatic structures. Compact PAHs and peri-condensed PAHs contribute to physical association; resonance-stabilized radicals, radical PAHs, and high-mass intermediates contribute to chemical stabilization [7-18].

The specific advantage of NDMS in soot modeling is that it allows physical and chemical inception mechanisms to be coupled without forcing a false choice between them. PAH association creates locally dense transient clusters. Radical chemistry and structural aging determine whether those clusters persist. Therefore, soot inception is represented as a transition controlled by both cluster lifetime and stabilization probability.

6.2 Inorganic nanoparticles

For inorganic flame particles, NDMS should be translated into the language of reactive oxide-cluster formation. The precursor pool may include metal-organic fragments, metal hydroxides, metal oxides, suboxides, chloride or alkoxide fragments, and small molecular clusters. Association may arise from collision, polarity, ionic or partially ionic interactions, and supersaturation. Stabilization may arise from oxidation, hydrolysis, condensation, ligand removal, oxygen incorporation, structural rearrangement, and crystallization [19-27,38-41].

A concrete example is TiO_2 formation. The gas phase may contain titanium-containing precursor fragments, partially oxidized titanium species, hydroxylated titanium intermediates, ligand-bearing fragments, small Ti-O clusters, and oxidizers such as O, OH, O_2, or H_2O. In an NDMS formulation, these species define a reactive precursor pool rather than converting immediately into stable TiO_2 particles. The transient cluster is not assumed to be crystalline TiO2; it may contain incomplete oxidation, residual ligands, hydroxyl groups, oxygen vacancies, or disordered Ti-O connectivity. Stabilization corresponds to ligand removal, oxygen incorporation, Ti-O-Ti network formation, dehydration, structural rearrangement, and the earliest persistent oxide structure.

The inorganic extension should therefore be interpreted cautiously. In the present framework, NDMS is not proposed as evidence that all flame-synthesized oxides pass through the same microscopic pre-particle state as soot. Rather, it provides a modeling architecture for representing reversible subcritical clustering followed by system-specific chemical or structural stabilization. The carbonaceous case

currently has more direct mechanistic support because PAH association, aromatic clustering, radical stabilization, and incipient soot structures are well documented in the soot literature. For inorganic nanoparticles, the corresponding NDMS-like variables and rate parameters must be defined separately for each precursor system, such as TiO_2, SiO_2, Al_2O_3, ZrO_2, or mixed oxides, according to the relevant precursor decomposition, oxidation, hydrolysis, condensation, ligand-removal, sintering, and crystallization pathways.

A conceptual comparison of the carbonaceous and inorganic interpretations of the NDMS framework is provided in Appendix A.

7. Objective advantages of the NDMS closure

The NDMS framework adds value only if it provides more physical content than an empirical nucleation multiplier. Its advantages can be stated objectively.

- It gives physical meaning to the pre-particle source term. The model contains a transient cluster population with identifiable formation, dissociation, and stabilization pathways.
- It separates reversible association from persistent particle formation. A cluster may exist without becoming a particle, which is essential under high-temperature flame conditions.
- It couples physical clustering and chemical stabilization. Physical association increases local precursor density and repeated encounters; chemistry or structural transformation reduces volatility and creates persistence.
- It allows multi-precursor inception. Weighted precursor descriptors avoid overdependence on one selected PAH or one molecular fragment.
- It introduces mechanistic pressure and temperature sensitivity. Pressure, concentration, and temperature affect k_n^{on}, k_n^{off}, k_n^{loss}, and k_n^{stab} instead of appearing only as fitted corrections.
- It is compatible with existing tools. NDMS can be implemented in detailed chemistry, sectional PBEs, moment methods, or reduced CFD closures without discarding established soot or aerosol dynamics.
- It is falsifiable. The framework predicts that inception depends on cluster persistence and stabilization probability, not only on precursor concentration. This can be tested through onset, pressure dependence, early size distributions, precursor sensitivity, and cluster-sensitive diagnostics.

8. Parameterization and identifiability

The main risk of NDMS is over-parameterization. To avoid this, parameters must be introduced hierarchically and constrained independently where possible. A first-generation model should use one association-weighted precursor descriptor C_P^{assoc}, one stabilization-weighted descriptor C_P^{stab}, one transient cluster scalar Z, one association rate k^{on}, one dissociation rate k^{off}, one competing-loss rate k^{loss}, one stabilization rate k^{stab}, and one particle source J_{NDMS}. Additional cluster classes, density corrections, composition-dependent weights, or multiple stabilization pathways should be added only when they improve inception-specific observables without destroying identifiability.

Association parameters can be estimated from collision theory, sticking probabilities, quantum-chemical binding energies, and molecular-dynamics cluster sampling [7-10]. Dissociation rates can be constrained by detailed balance, association free energies, or high-temperature molecular simulations.

Stabilization rates can be linked to radical recombination, cross-linking, H loss, aromatization, oxidation, hydrolysis, ligand removal, or structural transformation kinetics, depending on the system [11-15,19-27].

Experimental calibration should focus first on observables that directly probe inception rather than mature particle properties. Reduced CFD closures should be calibrated only after plausible parameter ranges have been established by molecular calculations, detailed mechanisms, or targeted flame experiments. This sequence is necessary to keep NDMS as a physical closure rather than another empirical multiplier.

9. Validation, falsification, and diagnostics

NDMS should be evaluated against inception-specific observables. Mature soot volume fraction, final primary-particle diameter, or aggregate morphology are useful but insufficient because many different inception closures can be compensated by later growth, coagulation, or oxidation rates. The relevant tests are those that probe the transition region itself.

1. Particle onset location and onset temperature.
2. Pressure dependence of early particle number density [42, 43].
3. Near-threshold flame behavior where small changes in equivalence ratio, pressure, or residence time switch particle formation on or off [43, 44].
4. Early particle-size distributions below approximately 5 nm for soot.
5. Sensitivity to PAH classes, radical pools, oxidizers, and precursor fragments.
6. Molecular-beam or mass-spectrometric evidence of transient clusters or high-mass intermediates.
7. Spectroscopic shifts, broadening, or fluorescence signatures consistent with clustered aromatics.
8. Isotope-labeling evidence of precursor incorporation into early particles.
9. For inorganic systems, dependence of primary-particle size, composition, amorphous/crystalline character, and phase on precursor concentration, oxidizer environment, and residence time.

The hypothesis would be strengthened if a constrained NDMS closure improves these observables compared with direct empirical nucleation. It would be weakened if simpler direct-nucleation models reproduce the same inception-specific observables with equal or better accuracy using fewer independently fitted parameters, or if experiments show that cluster persistence and stabilization probability do not affect onset under the conditions studied.

10. Scope and limitations

NDMS should not be presented as a universal mechanism or as proof of a new condensed phase. It is a modeling abstraction for a transition state where transient clustering and stabilization are expected to matter. Its usefulness depends on system, temperature, pressure, precursor chemistry, and diagnostic evidence.

Several limitations must be acknowledged. First, additional variables and rate coefficients increase model complexity. Second, some parameters are difficult to measure directly. Third, precursor-descriptor weights can become arbitrary if not constrained. Fourth, the inorganic analogy must be developed case by case because oxide-cluster chemistry differs from aromatic clustering. Fifth, a reduced bounded factor may improve engineering models but cannot by itself reveal molecular mechanisms. These limitations do not invalidate the framework, but they define how it should be used: minimally, transparently, and with validation against inception-specific observables.

11. Conclusions

This paper formulates the transient nano-dense molecular state hypothesis as a persistence–stabilization closure for combustion nanoparticle inception. The framework addresses a specific weakness in current soot and inorganic flame-aerosol models: the conversion of reactive molecular precursors into the first persistent particle population. Instead of treating inception as an immediate irreversible jump from gas-phase chemistry to particle dynamics, the NDMS formulation represents this transition through three coupled processes: precursor association, cluster dissociation and other non-stabilizing losses, and chemical or structural stabilization.

The central modeling claim is that a transient cluster becomes relevant to particle formation only when its local population and residence time are sufficient for stabilization to compete with dissociation and other loss pathways. This leads naturally to an operational density-enhancement criterion, association- and stabilization-weighted precursor descriptors, reversible cluster balances, stabilization probabilities, and particle source terms that can be implemented at different levels of model resolution. In detailed simulations, NDMS may be represented by cluster master equations coupled to gas-phase chemistry. In sectional, moment, or CFD models, it may be reduced to bounded persistence–stabilization factors or transported pre-particle reservoirs.

For carbonaceous systems, the framework provides a structured way to couple PAH association, radical-containing precursor chemistry, covalent linking, hydrogen loss, aromatization, and chemical aging without forcing a choice between purely physical clustering and purely chemical growth. For inorganic flame-generated nanoparticles, the same architecture should be interpreted more cautiously as an analogous, system-dependent representation of reactive subcritical oxide-cluster formation, precursor transformation, ligand removal, oxidation, hydrolysis, condensation, structural rearrangement, and crystallization. The shared feature is therefore not identical chemistry, but a kinetic architecture in which reversible clustering precedes stabilization into persistent particles.

The usefulness of NDMS should ultimately be judged by falsifiable model performance. The framework would be strengthened if physically constrained NDMS closures improve inception-specific predictions such as particle onset, pressure dependence, early particle-size distributions, precursor sensitivity, and cluster-sensitive spectroscopic or mass-spectrometric diagnostics. It would be weakened if simpler direct-nucleation closures reproduce the same observables with fewer independently fitted parameters, or if experiments show that cluster persistence and stabilization probability are not kinetically relevant under the conditions studied. In this sense, NDMS is best viewed not as a replacement for existing soot or aerosol models, but as a testable closure for the molecular-to-particle transition that those models currently treat only approximately.

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References

[1] Frenklach, M. Reaction mechanism of soot formation in flames. Physical Chemistry Chemical Physics 2002, 4, 2028-2037.

[2] Wang, H. Formation of nascent soot and other condensed-phase materials in flames. Proceedings of the Combustion Institute 2011, 33, 41-67.

[3] Richter, H.; Howard, J. B. Formation of polycyclic aromatic hydrocarbons and their growth to soot: A review of chemical reaction pathways. Progress in Energy and Combustion Science 2000, 26, 565-608.

[4] Appel, J.; Bockhorn, H.; Frenklach, M. Kinetic modeling of soot formation with detailed chemistry and physics: Laminar premixed flames of C2 hydrocarbons. Combustion and Flame 2000, 121, 122-136.

[5] Marinov, N. M.; Pitz, W. J.; Westbrook, C. K.; Castaldi, M. J.; Senkan, S. M. Modeling of aromatic and polycyclic aromatic hydrocarbon formation in premixed methane and ethane flames. Combustion Science and Technology 1996, 116-117, 211-287.

[6] Saggese, C.; Frassoldati, A.; Cuoci, A.; Faravelli, T.; Ranzi, E. A wide-range kinetic modeling study of soot formation. Combustion and Flame 2014, 161, 1489-1501.

[7] Herdman, J. D.; Miller, J. H. Intermolecular potential calculations for polynuclear aromatic hydrocarbon clusters. Journal of Physical Chemistry A 2008, 112, 6249-6256.

[8] Totton, T. S.; Misquitta, A. J.; Kraft, M. A quantitative study of the clustering of polycyclic aromatic hydrocarbons at high temperatures. Physical Chemistry Chemical Physics 2012, 14, 4081-4094.

[9] Chen, D.; Totton, T. S.; Akroyd, J.; Mosbach, S.; Kraft, M. Size-dependent melting of polycyclic aromatic hydrocarbon nano-clusters: A molecular dynamics study. Carbon 2014, 67, 79-91.

[10] Faccinetto, A.; et al. Evidence on the formation of dimers of polycyclic aromatic hydrocarbons in a laminar diffusion flame. Communications Chemistry 2020, 3, 112.

[11] Johansson, K. O.; Head-Gordon, M. P.; Schrader, P. E.; Wilson, K. R.; Michelsen, H. A. Resonance-stabilized hydrocarbon-radical chain reactions may explain soot inception and growth. Science 2018, 361, 997-1000.

[12] Johansson, K. O.; et al. Radical-radical reactions, pyrene nucleation, and incipient soot formation in combustion. Proceedings of the Combustion Institute 2017, 36, 799-806.

[13] Rundel, J. A.; et al. Promotion of particle formation by resonance-stabilized radicals during hydrocarbon pyrolysis. Combustion and Flame 2022, 243, 111942.

[14] Elias, J.; et al. Investigation of resonance-stabilized radicals associated with soot particle inception using advanced electron paramagnetic resonance techniques. Communications Chemistry 2023, 6, 110.

[15] Mercier, X.; et al. Direct observation and identification of resonance-stabilized radicals in a sooting flame. Communications Chemistry 2025, 8, 295. DOI: 10.1038/s42004-025-01689-7.

[16] Commodo, M.; Kaiser, K.; De Falco, G.; Minutolo, P.; Schulz, F.; D'Anna, A.; Gross, L. On the early stages of soot formation: Molecular structure elucidation by high-resolution atomic force microscopy. Combustion and Flame 2019, 205, 154-164.

[17] Schulz, F.; Commodo, M.; Kaiser, K.; De Falco, G.; Minutolo, P.; Meyer, G.; D'Anna, A.; Gross, L. Insights into incipient soot formation by atomic force microscopy. Proceedings of the Combustion Institute 2019, 37, 885-892.

[18] Michelsen, H. A.; et al. A review of terminology used to describe soot formation and evolution under combustion and pyrolytic conditions. ACS Nano 2020, 14, 12470-12490.

[19] Pratsinis, S. E. Flame aerosol synthesis of ceramic powders. Progress in Energy and Combustion Science 1998, 24, 197-219.

[20] D'Anna, A. Combustion-formed nanoparticles. Proceedings of the Combustion Institute 2009, 32, 593-613.

[21] Kruis, F. E.; Kusters, K. A.; Pratsinis, S. E.; Scarlett, B. A simple model for the evolution of the characteristics of aggregate particles undergoing coagulation and sintering. Aerosol Science and Technology 1993, 19, 514-526.

[22] Buesser, B.; Pratsinis, S. E. Design of nanomaterial synthesis by aerosol processes. Annual Review of Chemical and Biomolecular Engineering 2012, 3, 103-127.

[23] Li, S.; Ren, Y.; Biswas, P.; Tse, S. D. Flame aerosol synthesis of nanostructured materials and functional devices: Processing, modeling, and diagnostics. Progress in Energy and Combustion Science 2016, 55, 1-59.

[24] Gebauer, D.; Cölfen, H. Prenucleation clusters and non-classical nucleation. Nano Today 2011, 6, 564-584.

[25] Vekilov, P. G. Nucleation. Crystal Growth & Design 2010, 10, 5007-5019.

[26] Dasappa, S.; Camacho, J. Thermodynamic barrier to nucleation for manganese oxide nanoparticles synthesized by high-temperature gas-to-particle conversion. Energy & Fuels 2021, 35, 1874-1884.

[27] Tsagkaridis, M.; et al. Modeling of silica synthesis in a laminar flame by coupling an extended population balance model with computational fluid dynamics. Aerosol Science and Technology 2023, 57, 296-317. DOI: 10.1080/02786826.2023.2166808.

[28] Saylam, A. A Transient Nano-Dense Molecular State in Nanoparticle Inception: Bridging Physical Clustering and Chemical Stabilization. Zenodo, 2026. DOI: 10.5281/zenodo.19730735.

[29] Kraft, M. Modelling of particulate processes in combustion. Proceedings of the Combustion Institute 2005, 30, 967-986.

[30] Frenklach, M. Method of moments with interpolative closure. Chemical Engineering Science 2002, 57, 2229-2239.

[31] Singh, J.; Patterson, R. I. A.; Kraft, M.; Wang, H. Numerical simulation and sensitivity analysis of detailed soot particle size distribution in laminar premixed ethylene flames. Combustion and Flame 2006, 145, 117-127.

[32] Mueller, M. E.; Blanquart, G.; Pitsch, H. Hybrid method of moments for modeling soot formation and growth. Combustion and Flame 2009, 156, 1143-1155.

[33] Hou, D.; Lindberg, C. S.; Manuputty, M. Y.; You, X.; Kraft, M. Modelling soot formation in a benchmark ethylene stagnation flame with a new detailed population balance model. Combustion and Flame 2019, 203, 56-71.

[34] Rigopoulos, S. Modelling of soot aerosol dynamics in turbulent flow. Flow, Turbulence and Combustion 2019, 103, 565-604.

[35] Leung, K. M.; Lindstedt, R. P.; Jones, W. P. A simplified reaction mechanism for soot formation in nonpremixed flames. Combustion and Flame 1991, 87, 289-305.

[36] Moss, J. B.; Stewart, C. D.; Syed, K. J. Flowfield modelling of soot formation at elevated pressure. Symposium (International) on Combustion 1988, 22, 413-423.

[37] Brookes, S. J.; Moss, J. B. Predictions of soot and thermal radiation properties in confined turbulent jet diffusion flames. Combustion and Flame 1999, 116, 486-503.

[38] Johannessen, T.; Pratsinis, S. E.; Livbjerg, H. Computational fluid-particle dynamics for the flame synthesis of alumina particles. Chemical Engineering Science 2000, 55, 177-191.

[39] Jossen, R.; Heine, M. C.; Pratsinis, S. E.; Mädler, L.; Stark, W. J. Morphology and composition of spray-flame-made yttria-stabilized zirconia nanoparticles. Chemical Engineering Science 2005, 60, 3079-3087.

[40] Groehn, A. J.; Pratsinis, S. E.; Wegner, K. Fluid-particle dynamics during combustion spray aerosol synthesis of ZrO2. Chemical Engineering Journal 2012, 191, 491-502.

[41] Tsantilis, S.; Pratsinis, S. E. Soft- and hard-agglomerate aerosols made at high temperatures. Langmuir 2004, 20, 5933-5939.

[42] Saylam, A. Behavior of premixed sooting flame in a high-pressure burner. *Reactions* 2023, *4*, 155–170. DOI: 10.3390/reactions4010009.

[43] Mi, X.; et al. Near-threshold soot formation in premixed flames at elevated pressure. *Carbon* 2021, *181*, 143–154. DOI: 10.1016/j.carbon.2021.05.014.

[44] Saylam, A.; et al. Influence of lateral species diffusion and heat transfer on the evaluation of near-threshold sooting flames. *Combustion and Flame* 2023, *253*, 112775. DOI: 10.1016/j.combustflame.2023.112775.

Appendix A. Conceptual comparison of carbonaceous and inorganic NDMS-type inception pathways

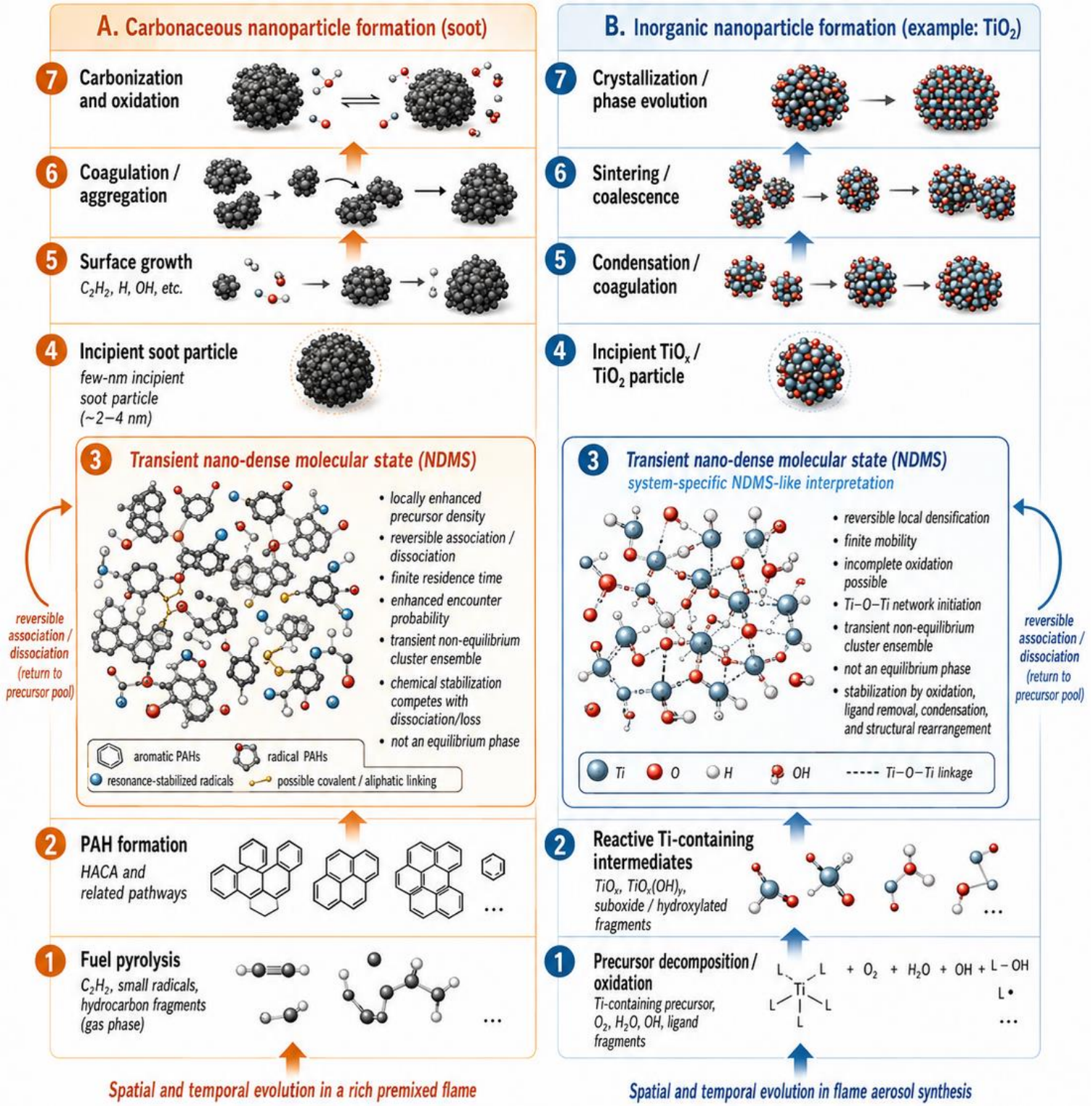

Figure A1. Conceptual comparison of carbonaceous and inorganic nanoparticle inception in combustion incorporating the transient nano-dense molecular state as an intermediate non-equilibrium regime. The schematic is illustrative and does not imply identical microscopic pathways for carbonaceous and inorganic systems. Rather, it shows a common modeling structure in which gas-phase precursors form a transient, reversible, non-equilibrium cluster regime before part of this population becomes persistent through chemical or structural stabilization.