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# Nanoparticle Inception via a Transient Nano-Dense Molecular State: Bridging Clustering and Chemical Stabilization

**Ahmad Saylam**

Independent Researcher – Applied Physical and Chemical Sciences
Duisburg, Germany
Corresponding author: saylamah@gmail.com

## Abstract

The formation of nanoparticles in combustion systems, including soot and selected inorganic materials, involves coupled physical and chemical processes that remain incompletely understood. Current descriptions tend to emphasize either gas-phase chemical growth pathways or physically driven clustering mechanisms.

This work proposes a testable, physically grounded hypothesis in which the inception of nanoparticles proceeds through the formation of a transient, non-equilibrium, nano-dense molecular state (NDMS), which is composed of precursor species. In this state, intermolecular interactions arising primarily from quantum-mechanical dispersion forces and configurational effects promote local densification and increase encounter lifetimes. Meanwhile, retained molecular mobility enables coalescence and enhances reactive stabilization. Subsequent chemical processes reduce volatility and progressively stabilize the evolving structure, leading to the formation of stable particles.

This hypothesis provides a continuous description of inception that links gas-phase chemistry and condensed-phase particle formation without the need for a strictly discrete nucleation event. It is consistent with several recent experimental and computational observations in soot formation. However, the relative contributions of physical clustering and chemical stabilization remain a matter of active debate. The applicability of this hypothesis to inorganic systems is discussed in the context of cluster-mediated particle formation.

The hypothesis also yields predictions that can be tested experimentally, concerning cluster lifetimes, spectroscopic signatures and deviations from classical nucleation behavior. Further quantitative experimental and computational studies are required to investigate the existence, properties, and kinetic relevance of the transient nano-dense molecular state (NDMS).

**Keywords:** Nanoparticle, inception, nucleation, soot, clustering, aggregation.

## 1. Introduction

The formation of nanoparticles in combustion involves a wide range of materials [2,4,11], including soot (carbonaceous), metal oxides (e.g. $TiO_2$, $SiO_2$) and other engineered nanomaterials. Despite the differences in their chemistry, a common challenge lies in understanding how gas-phase molecules transition to form stable condensed particles.

In the case of soot formation, this transition has traditionally been attributed to the growth and aggregation of polycyclic aromatic hydrocarbons (PAHs) [1-3,8], whereas in inorganic systems it is often described by classical nucleation theory. However, both approaches are limited under combustion conditions, where high temperatures, non-equilibrium chemistry and strong gradients dominate.

Recent experimental and computational studies suggest that the initial stages of particle formation may involve complex clustering phenomena, transient structures, and chemically active intermediates [3,9,10]. These observations highlight the need for a unified description that incorporates both physical clustering and chemical stabilization.

## 2. Limitations of Purely Physical or Chemical Views

### 2.1 Physical clustering models

Physical models attribute particle formation to clustering driven by dispersion interactions [6,7], such as van der Waals or π–π stacking. Quantum mechanical calculations demonstrate that dispersion interactions between polycyclic aromatic hydrocarbons (PAHs) can produce binding energies of several $k_B T$ for large aromatic systems [6,7]. However, at typical flame temperatures, the associated binding energies are comparable to or lower than the thermal energy of small molecular systems, resulting in limited cluster stability. Consequently, purely physical stabilization generally only occurs in sufficiently large species and/or in areas of high local concentration, where intermolecular interactions and collision frequencies are increased.

### 2.2 Chemical growth models

Chemical models describe the formation of bonds as arising from reactions involving reactive intermediates, such as radical recombination and H-abstraction–$C_2H_2$ addition [1,2,8]. These processes contribute to molecular growth and stabilization.

However, in dilute, high-temperature environments, the probability of reactive encounters may be reduced due to short interaction times and rapid diffusion, unless there are mechanisms to increase local concentrations or prolong interaction times.

## 3. Transient Nano-Dense Molecular State (NDMS) Hypothesis

### 3.1 Hypothesis statement

It is proposed that nanoparticle inception proceeds through the formation of a **transient, nano-scale, dense molecular state (NDMS)** characterized by:

- Elevated local concentration of precursor species (e.g., PAHs or reactive intermediates).
- Significant intermolecular interactions (dispersion, polarizability, π–π interactions).
- Finite molecular mobility (allowing rearrangement and coalescence).
- A lifetime exceeding binary collision times but shorter than that of stabilized particles.

In this context, “nano-dense” refers to a local molecular number density significantly higher than that of the surrounding gas phase, while remaining below bulk condensed-phase density.

From a thermodynamic perspective, this “state” is **not a distinct equilibrium phase**, but rather a **finite-size non-equilibrium ensemble of molecular clusters or a transient dense precursor-cluster pool**. The emergence of such a transient state can be interpreted through a simplified cluster free energy formulation [16,17]:

$$G(N) = N\mu_{gas} + \Delta G_{int}(N) - TS_{conf}(N)$$

Where $N$ is the number of molecules in the cluster, $\mu_{\mathrm{gas}}$ is the chemical potential of the precursor species in the gas phase, $\Delta G_{\mathrm{int}}(N)$ represents the intermolecular interaction contribution (primarily dispersion and π–π interactions), and $S_{\mathrm{conf}}(N)$ is the configurational entropy associated with molecular arrangements within the cluster.

For intermediate cluster sizes, the competition between attractive intermolecular interactions and configurational entropy can produce a shallow local minimum in free energy, corresponding to a metastable NDMS. Under combustion conditions, this minimum does not imply equilibrium stability, but rather a kinetically sustained state governed by ongoing molecular exchange. Typical interaction energies are expected to be on the order of a few $k_B T$ under flame conditions, sufficient to enable transient clustering but not long-term stability.

The lifetime of NDMS is therefore controlled by the balance between molecular association and dissociation processes and is expected to scale with pressure and precursor concentration:

$$\tau_{NDMS} \sim \frac{1}{k_{diss}}\left(1 + \frac{k_{assoc}}{k_{diss}}\right)$$

Where $k_{\mathrm{assoc}}$ and $k_{\mathrm{diss}}$ are the association and dissociation rate coefficients.

From a quantum-chemical perspective, PAH interactions are governed by dispersion and π–π stacking [6,7], with stabilization energies sufficient to support transient clustering at high temperatures, particularly in many-body environments.

### 3.2 Physical Origin and Conceptual Positioning

The formation of NDMS can be understood as resulting from a combination of transport, collision dynamics and intermolecular interactions. High collision frequencies, together with attractive interactions, promote repeated molecular encounters and transient association. Meanwhile, finite residence times within clusters increase the likelihood of re-encounters before dissociation.

NDMS differs from several related concepts used to describe early particle formation. Unlike liquid-like clusters, it does not represent a quasi-equilibrium condensed phase. Unlike PAH dimers or small oligomers, it describes a dynamic, many-body environment involving continuous association and dissociation. NDMS also precedes incipient soot particles, which exhibit reduced volatility and structural stabilization.

Furthermore, cluster-mediated and non-classical nucleation theories [17] invoke dense precursor states and are typically formulated under quasi-equilibrium assumptions, but they do not explicitly account for chemically reactive dynamics. Instead, the NDMS hypothesis describes a strongly non-equilibrium, chemically active regime in which physical clustering and chemical stabilization are intrinsically coupled.

Accordingly, NDMS should not be interpreted as a new phase, but rather as a transient regime that emerges from the interplay of transport, intermolecular interactions and reactive kinetics under combustion conditions.

### 3.3 Molecular mobility and internal dynamics

Within these clusters, molecules may retain significant rotational and translational mobility. This implies:

- An **enhanced probability of coalescence and internal rearrangement**, facilitated by molecular mobility within the cluster.
- **Extended residence times for reactive encounters**, due to repeated interactions within a confined environment.

These properties are better described in terms of **diffusion coefficients**, **relaxation times**, and **restructuring dynamics**, rather than macroscopic quantities such as **viscosity**.

Figure 1 provides a schematic summary of the proposed mechanism, offering a conceptual framework for the coupled physical and chemical processes involved in nanoparticle inception. In this representation, the transition from gas-phase precursors [1,2] to stable particles occurs via a transient, non-equilibrium regime characterized by locally dense molecular clustering. Within this regime, intermolecular interactions promote temporary association, while retained molecular mobility enables repeated encounters and structural rearrangement. This combination facilitates chemical stabilization and the progressive formation of persistent nanoparticles. The figure illustrates this intermediate state as a continuous transition between gas-phase chemistry and condensed-phase particle formation rather than as a distinct nucleation event.

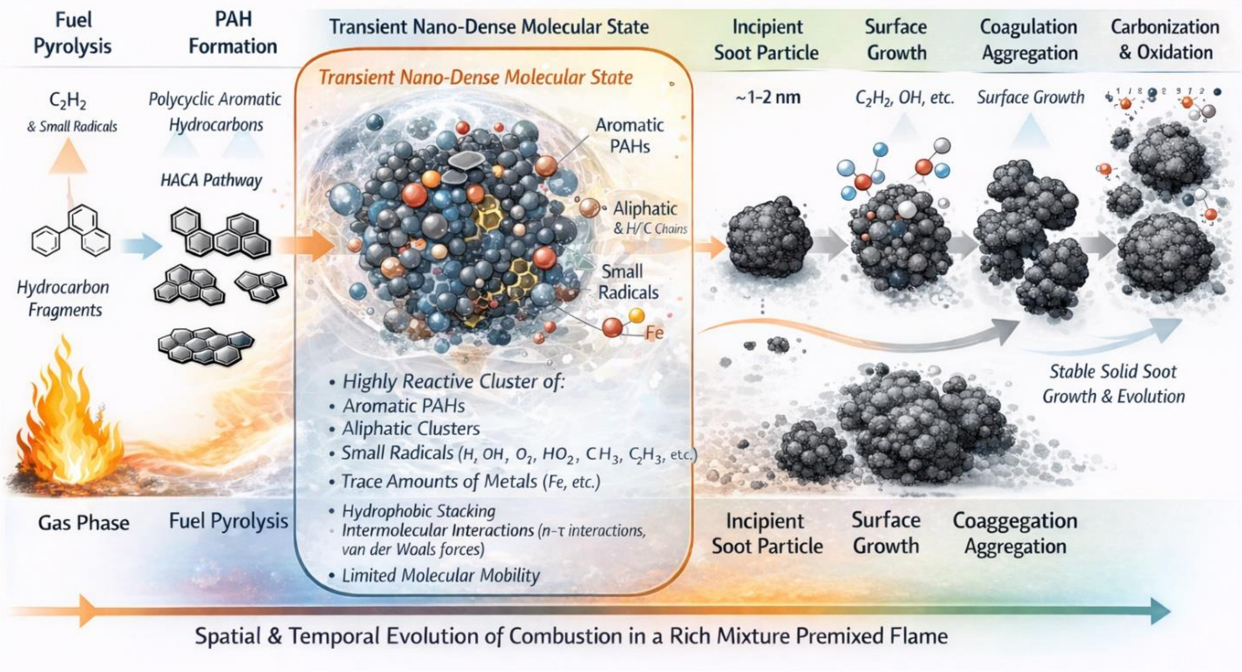

**Figure 1.** Schematic representation of nanoparticle inception in combustion incorporating the proposed transient nano-dense molecular state as an intermediate regime between gas-phase precursors and stable particles.

## 4. Coupling with Chemical Stabilization

Once a nano-dense molecular state forms, chemical reactions are facilitated by increased local concentration and reduced intermolecular separation [8,9]. Relevant processes include:

- **Radical recombination**, involving resonance-stabilized and other reactive intermediates [8].
- **Formation of covalent bridges** (e.g., aliphatic or cross-linking structures in soot precursors).
- **Structural rearrangements**, such as aromatization, ring condensation, and progressive carbonization [3,9].

These processes contribute to:

- **Reduced volatility**, through increased molecular weight and decreased vapor pressure.
- **Enhanced thermal stability**, associated with stronger bonding and structural ordering.
- **Evolution toward solid-like particles**, with decreasing molecular mobility.

Accordingly, particle inception can be interpreted as a coupled process involving:

1. **Physical densification** into a nano-dense molecular state.
2. **Chemical stabilization** into a persistent nanoparticle structure.

Structural rearrangements, such as aromatization, ring condensation, and progressive carbonization, reflect the evolution of the system toward lower free energy configurations. In the proposed transient nano-dense molecular state, enhanced local density and finite residence times enable these thermodynamically favorable transformations to proceed efficiently.

## 5. Generalization Beyond Soot

The proposed hypothesis is applicable to a broader range of combustion-generated nanoparticles beyond carbonaceous systems, provided that conditions allow for the formation of transient, locally dense molecular environments with finite residence times.

### 5.1 Inorganic nanoparticles

In combustion synthesis of metal oxide nanoparticles, particle inception is similarly preceded by the formation of molecular clusters derived from gaseous precursors (e.g., metal-organic or inorganic species). Under high-temperature conditions, frequent collisions and intermolecular interactions can lead to transient local densification of these species [11-12], analogous to the nano-dense molecular state proposed for soot precursors. Subsequent evolution may involve:

- **Cluster growth through collisions and condensation,** leading to dense, liquid-like or amorphous intermediates.
- **Phase transformation processes,** including oxidation, decomposition, and restructuring.
- **Crystallization and solidification,** resulting in thermodynamically stable particles.

While the specific chemical pathways differ from those in carbonaceous systems, the presence of transient, many-body molecular environments with enhanced local density and finite mobility suggests a mechanistic analogy to the proposed NDMS.

### 5.2 Common features across systems

Across both soot and inorganic nanoparticle formation, several common features can be identified:

- **Transition from gas-phase precursors to dense molecular clusters**, driven by collisions and intermolecular interactions.
- **Emergence of phase-like behavior at the nanoscale**, with clusters exhibiting liquid-like or amorphous characteristics.
- **Finite molecular mobility within clusters**, enabling repeated encounters and structural rearrangement.
- **Chemical transformation and stabilization**, whereby reactive processes convert transient clusters into persistent solid particles.

These shared features suggest that the NDMS concept may represent a general non-equilibrium regime of particle inception, arising when intermolecular interaction energies and collision frequencies are sufficient to sustain transient clustering on timescales longer than binary collisions.

### 5.3 Scope and limitations

However, the applicability of the nano-dense molecular state concept depends on the specific system and precursor chemistry. In particular, NDMS formation is expected to require:

- Sufficient precursor concentration or pressure to enable sustained clustering.
- Intermolecular interactions strong enough to compete with thermal dissociation.
- Reaction pathways capable of stabilizing transient clusters.

In systems where these conditions are not met, clustering may remain short-lived and insufficient to drive particle inception. The NDMS concept should therefore be considered system-dependent rather than universal.

The influence of pressure and flow configuration provides additional evidence for this system dependence. Experimental and numerical studies of premixed sooting flames in high-pressure burners demonstrate that increasing pressure enhances precursor formation, nucleation, and particle growth processes, often leading to a power-law increase in soot volume fraction [18]. At the same time, burner geometry and flow non-uniformities can modify local temperature and species distributions, thereby affecting the spatial development of soot formation zones.

These observations indicate that the persistence and properties of transient dense molecular environments are governed by the coupled effects of pressure, transport processes, and reactor configuration.

## 6. Implications

This perspective suggests several implications for the interpretation and modeling of nanoparticle inception:

- **Inception may be described as a continuous nanoscale transition**, involving progressive densification and structural evolution rather than a discrete nucleation event.
- **Classical nucleation theory may require extension**, particularly to account for non-ideal, chemically reactive clusters and deviations from equilibrium assumptions.
- **Modeling approaches should incorporate coupled physical and chemical processes**, including:
    - ✓ **Cluster thermodynamics**, determining stability, phase behavior, and the balance between association and dissociation under combustion conditions [16,17].
    - ✓ **Molecular mobility and internal transport within clusters**, influencing coalescence, structural rearrangement, and mass redistribution.
    - ✓ **Coupled physical–chemical kinetics**, describing the interplay between clustering dynamics, reactive pathways, and the progression toward stable particle formation.

## 7. Interpretation of Nucleation Flames within the NDMS Hypothesis

In experimental studies, Pascale Desgroux and her colleagues, including A. Faccinetto and X. Mercier, introduced the concept of nucleation flames [13]. These are defined as low-pressure premixed flames in which soot particle inception occurs, while subsequent growth processes, such as coagulation and surface growth [3,5], remain limited. These configurations allow the transition from gas-phase precursors to the first detectable particles to be investigated under conditions where later-stage evolution is minimized.

Measurements in such systems indicate that soot formation occurs shortly after the peak concentration of polycyclic aromatic hydrocarbons (PAHs) [14], resulting in the creation of extremely small primary particles, typically measuring 2–4 nm. Comparative studies with flames exhibiting significant soot growth have shown that these conditions isolate the early stages of particle formation and the associated chemical pathways.

The hypothesis proposed in this study suggests that these observations correspond to conditions near the threshold for the formation of a transient nano-dense molecular state. At the PAH concentration peak, increased collision frequency and intermolecular interactions promote the formation of locally dense molecular clusters with finite lifetimes. These transient clusters provide enhanced residence times and repeated intermolecular encounters, facilitating initial chemical stabilization processes.

However, under the low-pressure conditions characteristic of nucleation flames, the lifetime and spatial extent of such nano-dense molecular states remain limited. Consequently, while the formation of the first stabilized nanoparticles is enabled, the persistence of dense molecular environments necessary for continued coagulation and surface growth is reduced. This results in the formation of small particles that do not grow significantly thereafter.

By contrast, more strongly sooting flames can be understood as occurring in conditions where nano-dense molecular states persist over time and space, enabling ongoing clustering, chemical stabilization and particle growth.

Figure 2 illustrates this conceptual distinction between the nucleation and sooting regimes within the nano-dense molecular state hypothesis.

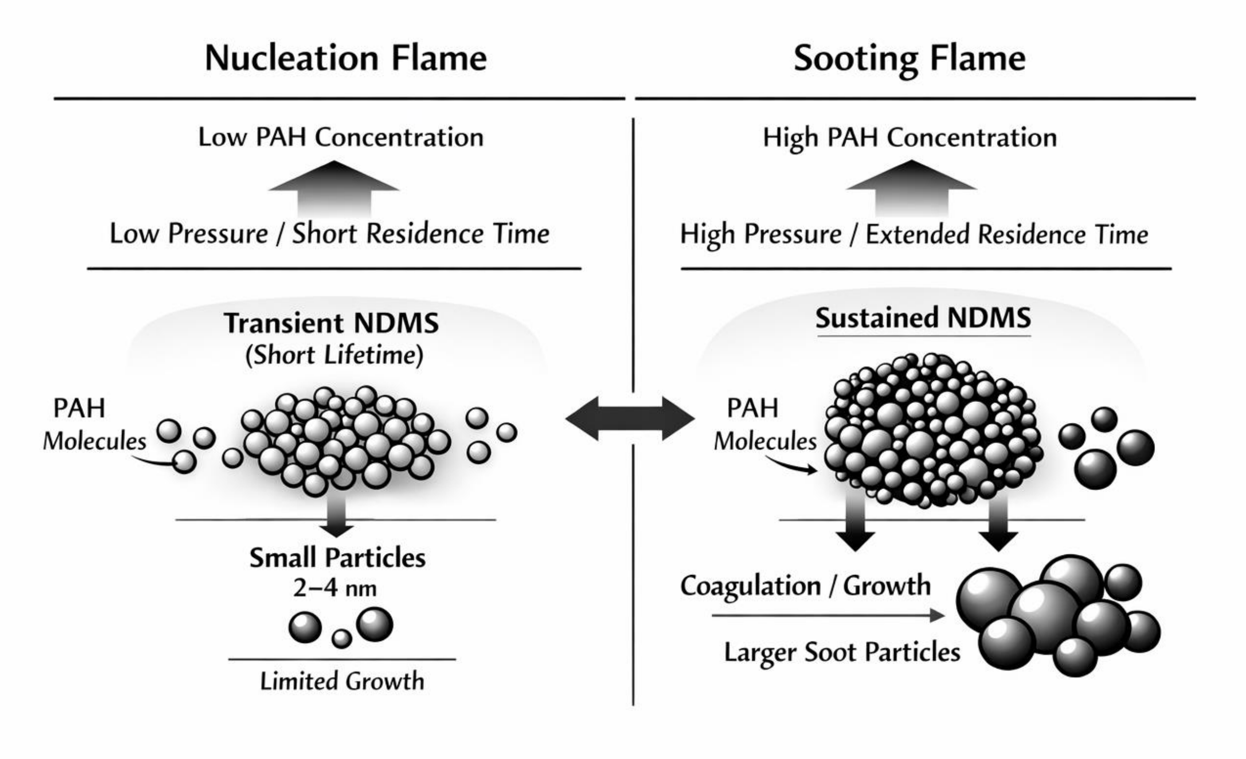

**Figure 2.** Conceptual comparison of nucleation flames and sooting flames interpreted within the transient nano-dense molecular state (NDMS) hypothesis.

Accordingly, nucleation flames can be viewed as probing a regime close to the onset of the formation of a nano-dense molecular state, providing an experimental insight into the earliest stages of nanoparticle formation. This suggests that the transition between the nucleation and sooting regimes may depend on the persistence and spatial extent of nano-dense molecular states under specific thermochemical conditions.

Additional experimental evidence from near-threshold premixed flames further supports the interpretation proposed here. Studies of ethylene/air flames at and slightly above the soot formation threshold have shown that soot inception occurs in a regime where formation and oxidation processes are closely balanced, leading to strong sensitivity to pressure, temperature, and local composition [19]. In particular, measured soot volume fractions and particle sizes exhibit pronounced dependence on pressure and equivalence ratio, while remaining confined to a narrow spatial region near the flame front. Furthermore, recent investigations have demonstrated that lateral species diffusion and heat transfer can significantly modify local thermochemical conditions in near-threshold flames, thereby influencing the onset of soot formation [20]. These observations are consistent with the NDMS hypothesis, in which transient, locally dense molecular environments with finite lifetimes govern the transition from gas-phase precursors to the first stabilized particles.

## 8. Testable Predictions of the NDMS Hypothesis

The nano-dense molecular state (NDMS) hypothesis leads to a set of specific, experimentally and computationally testable predictions. These predictions arise from the combined effects of enhanced local density, finite molecular mobility, and coupled physical–chemical processes within transient molecular clusters.

- ✓ **Cluster lifetime scaling**: The lifetime of NDMS-associated clusters is expected to increase with precursor concentration and pressure, reflecting the balance between molecular association and dissociation processes. This scaling may be probed experimentally using time-resolved diagnostics (e.g., pump–probe spectroscopy or molecular beam sampling) and is expected to exhibit a monotonic dependence on local number density [9,14].
- ✓ **Enhanced reaction rates:** Reaction rates within NDMS are expected to exceed those predicted for isolated gas-phase species, due to increased local density and repeated intermolecular encounters within transient clusters [8]. This enhancement may be quantified by comparing measured reaction rates with gas-phase kinetic models, with deviations indicating cluster-mediated reactivity.
- ✓ **Non-classical cluster size distributions:** Early-stage cluster populations are expected to exhibit fluctuating and non-monotonic size distributions, without a sharply defined critical nucleus as predicted by classical nucleation theory. Such distributions may be detected using high-resolution mass spectrometry or molecular beam techniques, and would differ from the smooth, monotonic distributions predicted by classical nucleation models [3,17].
- ✓ **Spectroscopic signatures of clustering:** Spectroscopic measurements are expected to reveal signatures of intermolecular interactions, such as broadened or shifted spectral features associated with transient molecular aggregation. These effects may be observable via laser-induced fluorescence (LIF), infrared spectroscopy, or Raman diagnostics, indicating the presence of clustered molecular environments.
- ✓ **Spatial localization in combustion systems:** NDMS formation is expected to occur preferentially in localized regions with high precursor concentrations, such as near the peak of PAH distributions in nucleation flames. Spatially resolved diagnostics (e.g., LII, LIF, or MBMS) may reveal localized zones of enhanced clustering preceding particle formation.
- ✓ **Threshold behavior:** A minimum precursor concentration or pressure is expected to be required for sustained NDMS formation, below which clustering remains transient and does not lead to particle inception. This threshold behavior may be identified experimentally by varying pressure or fuel composition and observing the onset of stable particle formation.

Together, these predictions provide a basis for evaluating the existence, properties, and kinetic relevance of the NDMS through combined experimental diagnostics and molecular-level simulations.

## 9. Conclusion

The formation of nanoparticles during combustion can be interpreted as the emergence of a transient nanoscale dense molecular state (NDMS), defined as a transient reactive cluster regime or mesoscopic non-equilibrium cluster ensemble, in which the molecular precursors densify progressively while retaining some mobility. According to this hypothesis, physical interactions facilitate local concentration and clustering, while chemical processes stabilize the evolving structure through bond formation and structural transformation.

This perspective provides a unified description of nanoparticle formation, explicitly linking gas-phase chemistry and condensed-phase particle formation via a continuous, non-equilibrium transition rather than requiring a discrete nucleation event. Thus, the NDMS concept offers a mechanistic bridge between physically driven clustering and chemically driven stabilization processes. In this context, the NDMS hypothesis provides a physically grounded framework for interpreting experimentally observed deviations from classical nucleation behavior in combustion systems.

This hypothesis is consistent with observations across carbonaceous and inorganic systems, and is supported by a set of experimentally and computationally testable predictions. These include the characteristic scaling of cluster lifetimes, deviations from classical nucleation behavior and spectroscopic signatures of transient molecular aggregation [17].

While the proposed framework does not replace existing models, it provides a complementary perspective that could contribute to more comprehensive descriptions of nanoparticle formation under combustion conditions [2,3]. Incorporating coupled physical–chemical dynamics and transient clustering effects, for example, could enhance the predictive capability of future models.

Further experimental and computational investigations are required to quantify the properties, dynamics and kinetic relevance of nano-dense molecular states and assess their role in different precursor systems and thermochemical conditions.

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