### Towards integrated modeling of methane pyrolysis and carbon material synthesis.

A. Khrabry<sup>1</sup>, Y. Barsukov<sup>2</sup>, L. Hoffenberg<sup>3</sup>, <u>I.D. Kaganovich<sup>2</sup> and D. Graves<sup>2,3</sup></u>

<sup>1</sup> Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, USA <sup>2</sup> Princeton Plasma Physics Laboratory, Princeton, NJ, USA

<sup>3</sup> Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ, USA

**Abstract:** Methane pyrolysis can be used for the large-scale production of hydrogen and valuable carbon co-products. In order to optimize the process, we are developing an integrated model of methane pyrolysis which consists of several sub-models including gasphase chemistry, soot formation, nucleation and growth of catalytic nanoparticles from metal vapor, and carbon nanotube synthesis on the catalyst particle surface.

Keywords: Methane pyrolysis, soot formation, condensation, catalytic nanoparticles.

# 1. Integrated chemical mechanism of methane pyrolysis and soot formation

Methane pyrolysis has demonstrated its potential for large-scale production of hydrogen (a.k.a. turquoise hydrogen) and valuable carbon co-products such as carbon black [1] and carbon nanotubes (CNTs) [2]. We are focusing on the CNT synthesis as CNTs are the more valuable carbon product. In CNT synthesis from methane pyrolysis, it is important to avoid soot formation because soot is an un-desirable by-product that consumes carbon from the feedstock and contaminates the product. The search for optimal methane pyrolysis conditions (reactor inlet gas mixture composition, temperature profile, etc.) requires a reliable chemical model describing both gasphase chemistry and soot formation. Multiple chemical reaction sets for methane pyrolysis can be found in literature (e.g. [3, 4, 5, 6]). We have implemented these reaction sets in a plug flow reactor model in Cantera chemical solver [7] and compared such obtained modeling results to available experimental data on methane pyrolysis in stationary and plug-flow reactors [8, 9]. The so-called ABF model [4] showed good agreement with the experimental data for methane conversion in a heated-wall flow reactor [8], as shown in Fig. 1, similar to previous studies [10].

However, agreement between the modeling results and experimental data is only observed when soot or other forms of solid carbon do not form. When solid carbon (soot or other structures) formed, there was a noticeable disagreement between the ABF modeling results and experimental data (e.g., the model overpredicted the formation of acetylene because carbon conversion to soot was not accounted for). It is clear that the mechanism needs to be expanded to incorporate better modeling of soot formation.

Soot particles form as agglomerates of large polycyclic aromatic hydrocarbons (PAHs) of 2-3 nm in diameter [11, 12]. There are multiple chemical mechanisms of small PAH formation (up to A7, i.e., coronene) available in literature, see, e.g., reviews [13, 14]. Most of these models are based on so-called hydrogen abstraction carbon (or acetylene) addition (HACA) [15] and hydrogen abstraction vinylacetylene addition (HAVA) [16] mechanisms.



Fig. 1. Methane conversion degree as a function of residence time for several flow temperatures in the flow of methane premixed with hydrogen (H<sub>2</sub>:CH<sub>4</sub> = 2:1) in a heated wall reactor [8]. Black lines – experimental data, color lines – modeling results using the ABF mechanism.



Fig. 2. The fraction of acetylene converted to soot in the flow in the flow of 30 000 ppm  $C_2H_2$  diluted in  $N_2$  in a heated wall reactor [18] as a function of temperature. Black line – experimental data, blue line – modeling.

We have integrated these models with the ABF mechanism and expanded them to include most prominent PAH species up to A40 (~2 nm in diameter) using forward reaction rates from HACA and HAVA mechanism reversed reaction rates based on thermodynamic data from NIST [17]. The predictions of the resulting mechanism are compared with experimental data [18] for acetelene conversion to soot in Fig. 2. In the model, soot was defined as the total of all PAH species larger than benzene.

## 2. Kinetic model of metal nanoparticle nucleation and growth

Nanoparticles of liquid metal serve as catalysts for the synthesis of carbon nanotubes (CNTs). In floating catalyst carbon vapor deposition (FCCVD) reactors, catalyst nanoparticles are usually synthesized directly in the flow of a cooling gas containing metal vapor, as in Refs. [19, 20]. Obtaining nanoparticles of a certain size with a narrow size distribution is a crucial step in the selective synthesis of CNTs of desired diameter, chirality, and number of walls.

The process of liquid metal nanoparticle formation from a supersaturated vapor is typically divided in two stages: nanoparticle nucleation (a.k.a. a nucleation burst) and coagulation, which is longer. Agglomeration also occurs later on after the particles solidify. It is known that condensation in a cooling vapor does not happen when the temperature reaches immediatelv the condensation temperature. There is a time lag for the vapor to reach a certain degree of supersaturation after which condensation happens rapidly with vapor density dropping and particle (cluster) density rising (see shaded area in Fig. 3) – hence the name 'nucleation burst'. The delay in the cluster formation occurs due to the nucleation energy barrier: particles below some critical size are thermodynamically unfavorable. This barrier becomes smaller as the supersaturation increases, eventually leading to a nucleation burst. The size of particles formed at the nucleation stage depends on both the cooling rate and the initial partial pressure of the metal vapor. The final size of the nanoparticles after the coagulation phase depends on the initial vapor density and the residence time (how long the particles collide with each other to form larger and larger coagulates until they solidify).

Dynamics of the size distribution of forming particles can be described by the so-called General Dynamics Equation (GDE) [21]. This is an integro-differential equation that is difficult to solve. There are simplified models of condensation based on the moments of the particle size distribution function. The most accurate model of nucleation was developed by S. Friedlander [22]. Based in this model, we have derived an analytical solution [23] for the nucleation delay, average nanoparticle size, and dispersion of the size distribution function after the nucleation burst as a function of cooling rate and vapor density (assuming linear gas cooling with time). These analytical expressions are a useful tool for quick assessment of nanoparticle properties. However, the Friedlander's nucleation model does not account for the coagulation of nanoparticles nor the smallest subcritical nanoparticles (i.e., the formation of nanoparticles that have not yet surpass the nucleation energy barrier).

Even though a simple nucleation model coupled with a mono-disperse coagulation model (as we have done prior in the modeling of carbon nanoparticle formation in the effluent of an arc discharge [24]) can predict average nanoparticle size with an error of about a factor of three. For the synthesis of CNTs with the desired characteristics, more precise knowledge of the nanoparticle size distribution is required.

In this paper, we present results obtained with a new computational condensation code. This code solves the full General Dynamics Equation (GDE) for the particle size distribution function, accounting for both nucleation and coagulation of particles. Coagulation is modeled in the free molecular regime because the size of the forming particles (several nm) is much smaller than the mean free path  $(\sim 1 \mu m)$ . The model is 0D (i.e., it is a plug-flow model). Unlike its predecessors (NGDE code [25] or the Friedlander's nucleation model, which do not consider particles below critical size), this code resolves the particle size distribution in the whole range of particle sizes. The model starts from monomers and does not limit the size of the computational grid. A special "non-diffusive" numerical scheme is used to avoid "smearing" of the particle size distribution from numerical diffusion that is typical in the NGDE scheme. Technical details of the numerical solution procedure will be provided in ensuing publications.



Fig. 3. Time history of vapor density (a) and particle density (b) during condensation of aluminum vapor.

In Fig. 3, modeling results obtained with our code (blue line) and with the Friedlander's model (orange line) are compared for the condensation of aluminum vapor starting from saturation conditions at 1,500°C with a constant cooling rate of  $10^6$  K/s. As can be seen from Fig. 4a, gas density starts decreasing much earlier in the full GDE solution obtained with our code compared to the Friedlander's model; consequently, the nucleation burst is slightly smoothened out and delayed. The reason for the deviation is the formation of sub-critical particles which is ignored in the Friedlander's model. Even though there is a small number of sub-critical particles compared to the total number of particles after the nucleation burst, they still consume a notable amount of the monomer gas. With the lower vapor density in the full solution, smaller particles form and the density of nascent particles is considerably higher, as is shown on Fig. 4b.

The nanoparticle formation model was validated by comparing to the asymptotic self-similar solution by S.K. Friedlander [21] (see Fig. 4). This semi-analytical solution represents particle size distribution as a final stage of a long coagulation process when the size distribution in normalized coordinates (divided by the total density of all clusters and average number of atoms in a cluster) stops changing with time. The modeling was performed for condensation of the iron vapor under the experimental conditions (temperature profile, vapor pressure) of Ref. [19]. The residence time was increased to allow the solution to equilibrate. As can be seen from Fig. 4, the numerical solution substantially deviates from the selfsimilar solution initially (as expected) but then gradually approaches it as the coagulation proceeds.



Fig. 4. Developing particle size distribution in normalized coordinates under conditions of experiments [19] – color lines; self-similar solution of S.K. Friedlander [21] – black line.

The results presented above (as well as most of the condensation research to date) were obtained using a spherical approximation for the nanoparticle shape, which has been used in most of the condensation simulations to date. With this approximation, the Gibbs free energy of formation of a particle,  $\Delta G = -NkT lnS + 4\pi \sigma r_W^2 N^{2/3}$  is derived from the saturation degree S and surface tension for a flat surface  $\sigma$  (here, N is the number of atoms in the particle,  $r_W$  is Wigner-Seitz radius). This approximation should work well for large particles (having a least a hundred atoms); however, for smaller particles its applicability is questionable. Gibbs free energies of formation for aluminum particles up to 50 atoms can be found in Ref. [26]. These values deviate from the spherical model with peaks and dips corresponding to so-called 'magic numbers' of atoms in a particle. Fig. 5a shows simulated particle size distributions for multiple time instants using the Gibbs free energies from Ref. [26], for the same conditions as in Fig. 4. The results clearly illustrate the effect of 'magic numbers' on the particle size distribution. Fig. 5b shows a drastic effect of the Gibbs free energy model on the condensation process: the spherical model predicts the condensation happening much earlier than with inclusion of 'magic numbers'.



Fig. 5. Particle size distributions for various time instants
(a) and vapor density evolution (b) during condensation of aluminum. Thick line – using the Gibbs free energies from Ref. [26], thin line – using the spherical model.



Fig. 6. Snapshots of an Fe<sub>13</sub> cluster at different temperatures in LAMMPS [28] MD simulations.

There are ongoing debates whether 'magic numbers' should be accounted for in the condensation process. The argument against 'magic numbers' is that the particles are not solid but are in a liquid state and thereby don't have an ordered structure [27]. Our molecular dynamics (MD) modeling using LAMMPS software package [28] qualitatively supports this statement: compare the Fe<sub>13</sub> cluster configuration at 0K and 1200K (solid state) with its appearance at 1500K (melting) in Fig. 6. This question remains open, and our modeling results show that there is a need for accurate thermodynamic data for small particles. We have started such a computational study for iron nanoparticles. We are using classical MD, ab-initio MD (AIMD), and density function theory (DFT) methods to calculate the Gibbs free energy of formation of many cluster sizes. The combination of different methods allows us to take into account the 'magic numbers' related to the electronic structure and packing of the clusters. As an example, Fig. 7a shows total energy of an Fe<sub>13</sub> cluster as a function of temperature calculated by classical MD (using LAMMPS) and AIMD with the PBE0 DFT functional in VASP software package [29]. As shown in Fig. 7b, a good agreement between the Finnis-Sinclair potential [30] and PBE0 functional on the binding energy per atom of Fe<sub>n</sub> clusters was obtained, while the HSE06 functional implemented in the Gaussian-16 code [31] predicts lower binding energy. Validation of the DFT functionals and MD

potentials for  $Fe_n$  clusters will be done via comparison to available experimental data on atom abstraction energies.



Fig. 7. Total energy of Fe<sub>13</sub> cluster as a function of temperature (a); the binding energy per atom of Fe<sub>n</sub> clusters calculated by the HSE06, PBE0 DFT functionals and by the Finnis-Sinclair potential (b), where the dashed line is the cohesive energy of (110) oriented surface of  $\alpha$ -Fe, the dash-dotted line is cohesive energy of  $\alpha$ -Fe bulk calculated by PBE0 functional (VASP).

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### References

- [1] L. Fulcheri, Int. J. Hydrog. Energy 48, 2920 (2023).
- [2] M. Pasquali & C. Mesters, *Proc. Natl. Acad. Sci.*, **118**, e2112089118 (2021).
- [3] J.R. Fincke et al, Ind. Eng. Chem. Res. 41, 1425 (2002).
- [4] J. Appel et al, *Combust. Flame* **121**, 122 (2000).
- [5] Y. Hidaka et al, Combust. Flame 118, 340 (1999).

- [6] G. Smith, <u>combustion.berkeley.edu/gri-mech/</u>, (1999).[7] <u>https://cantera.org/</u>
- [8] O. Olsvik et al., Chem. Eng. Technol. 18, 349 (1995).
- [9] C.-J. Chen et al., Can. J. Chem. 53 (1975).
- [10] M. Sinaki et al, Int. J. Hydrog. Energy 36, 2936 (2011).
- [11] P. Duvvuri et al, In: A.K. Agarwa et al., (eds) Engine exhaust particulates. Springer Singapore, 71–119.
- [12] M. Gautier et al, Int. J. Hydrog. Energy 42, 2814 (2017).
- [13] H. Tao et al, *Fuel* **255**, 115796 (2019).
- [14] E. Reizer et al, *Chemosphere* **291**, 132793 (2022).
- [15] M. Frenklach et al, Symp. Combust. 20, 887 (1984).
- [16] G.M. Badger et al., J. Chem. Soc. 2449-2452 (1958).
- [17] T.C. Allison & D.R. Burgess Jr., NIST Special Publication 1186 (2015).
- [18] M. Ruiz et al, Ind. Eng. Chem. Res. 46 7550 (2007).
- [19] C. Hoecker et al, *Sci. Rep.* **7**, 14519 (2017).
- [20] K.S. Kim et al, Chem. Eng. J. 250, 331 (2014).
- [21] S.K. Friedlander, Smoke, Dust, and Haze: Fundamentals of Aerosol Dynamics (Oxford University Press, Oxford, 2000).
- [22] S.K. Friedlander, Ann. N. Y. Acad. Sci. 404, 354 (1983)
- [23] M. Tacu et al, Phys. Rev. E 102, 022116 (2020).
- [24] S. Yatom et al, MRS Commun. 8, 842-849 (2018).
- [25] A. Prakash et al, Aerosol Sci. Technol. 37, 892 (2003).
- [26] Z.H. Li et al, J. Phys. Chem. C 111, 16227 (2007).

[27] B.M. Smirnov, Cluster Processes in Gases and Plasmas (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010)

- [28] A.P. Thompson et al, *Comp. Phys. Comm.* **271**, 10817 (2022).
- [29] G. Kresse & J. Hafner, Phys. Rev. B 47, 558 (1993);
- G. Kresse & J. Furthmüller, Comput. Mat.Sci. 6, 15 (1996);
- G. Kresse & J. Furthmüller, Phys. Rev.B 54, 11169 (1996);
- G. Kresse & D. Joubert, Phys. Rev. 59, 1758 (1999).

[30] M.W. Finnis & J.E. Sinclair, *Phil. Mag. A* **50**, 45 (1984);

M.W. Finnis & J.E. Sinclair, *Phil. Mag. A* **53**, 161 (1986) [31] Gaussian 16, Revision A.03, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2016.