THE PHYSICS OF NANODUSTY PLASMAS

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Special Thanks to: Ed Thomas (Auburn U.)

Frontiers of Plasma Science Town Hall Meeting
June 30-July 1, 2015

UNIVERSITY OF MINNESOTA
Driven to Discover℠

OVERVIEW

- Macro-Dusty Plasmas
- Nano-Dusty Plasmas
    - Plasma-Nanoparticle Surface Interactions
    - Nanodusty Plasma Dynamics
    - Bridging the Pressure Gap
- Impact on Society
- Connectivity to Other White Papers

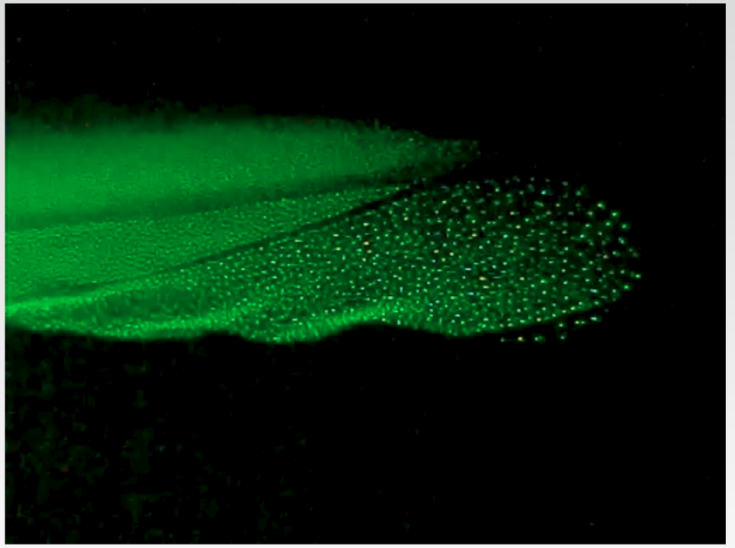
MACRO- Dusty (complex, fine particle, colloidal) plasmas

- Complex plasmas - four component plasma system
  - Ions
  - Electrons
  - Neutral atoms
  - MACRO- Charged microparticles(many to 10s μm)

- Plasma and charged microparticles - coupled via collection of ions and electrons from the background plasma.

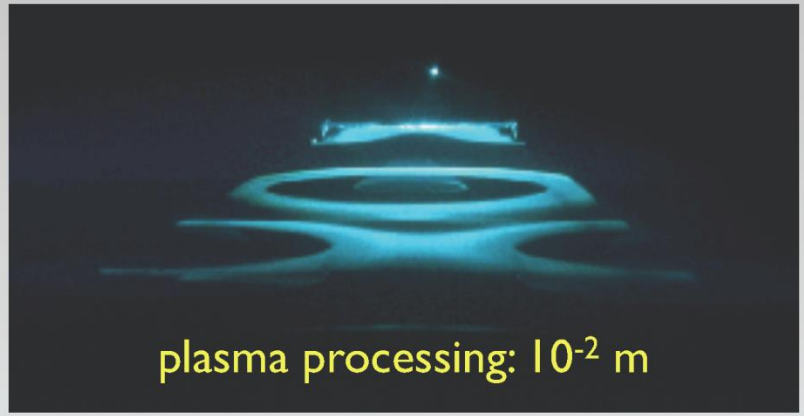
- Presence of microparticles:
  - Modifies density and charge distribution
  - Modifies plasma instabilities
  - Introduces new dust-driven waves

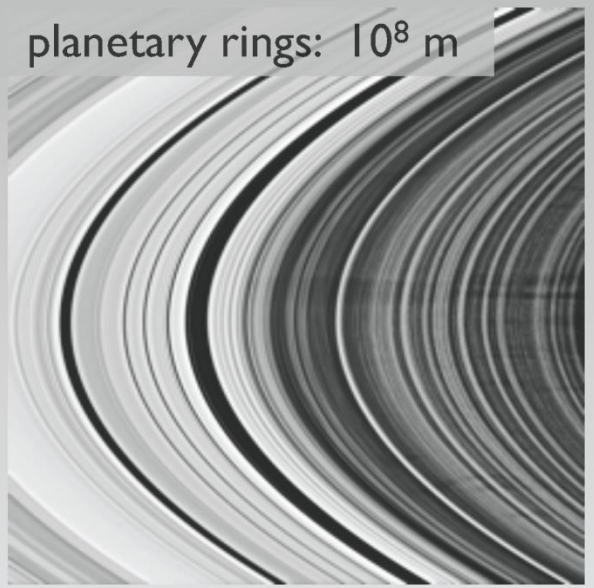
- Measurements of dust particles:
  - Forces
  - Electrostatic potential
  - Velocity distributions

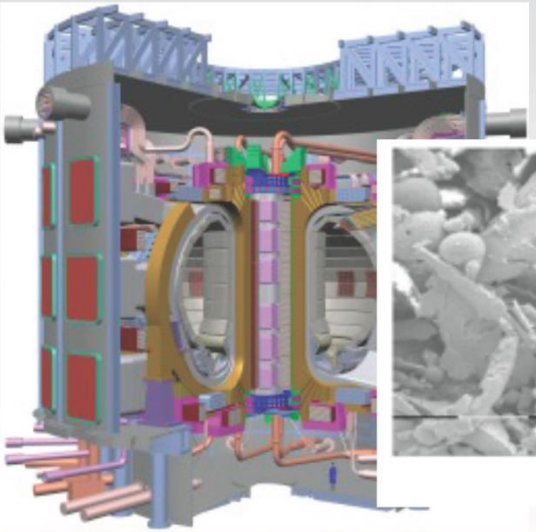


MACRO- Dusty plasmas cover a wide range of phenomena

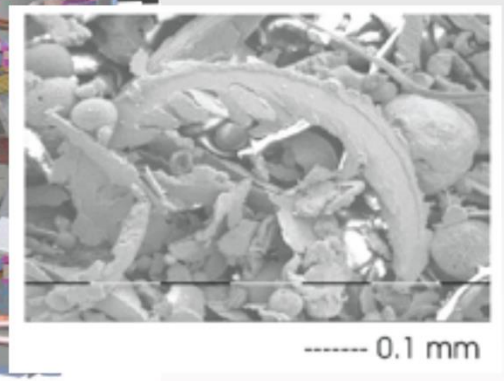
Because dusty plasmas are a topic of
<u>UNIVERSAL</u> interest.

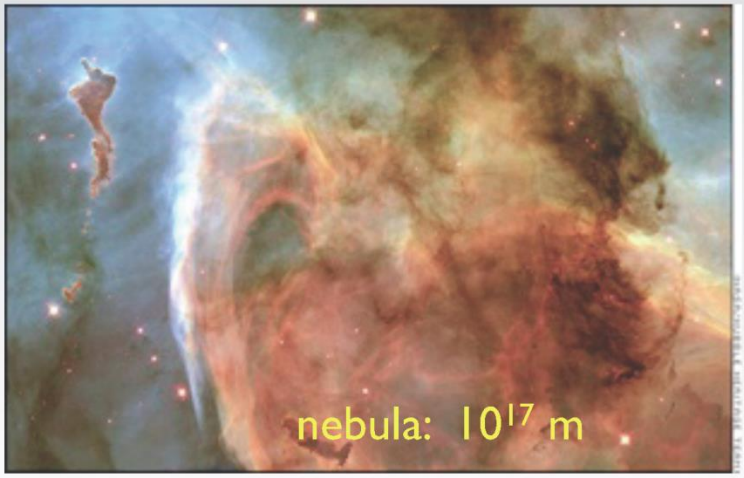




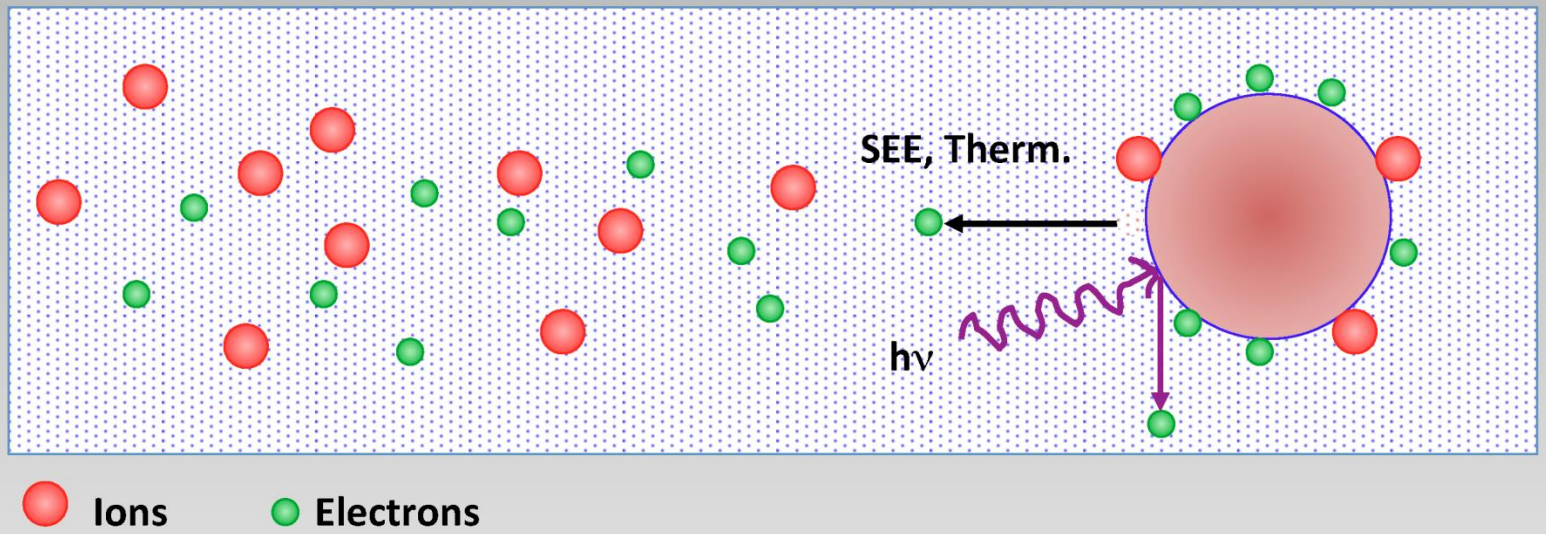


fusion: 10^{1} m





Key physics: Charging - Q_d is a new dynamic variable



- A dynamic equilibrium is established as the grain electrically floats in the plasma: $I_{total} = I_{electron} + I_{ion} + I_{see} + I_{thermionic} + I_{h\nu} = f(n_j, T_j, \varphi; \underline{r}, t)$
- Implication: $dQ_d/dt \neq$ constant
- Grain charge ($Q_d = Z_d e$) is a new dynamic variable
- In the laboratory, Q_d is negative. In space, Q_d can be positive or negative **(of macro-particles)**

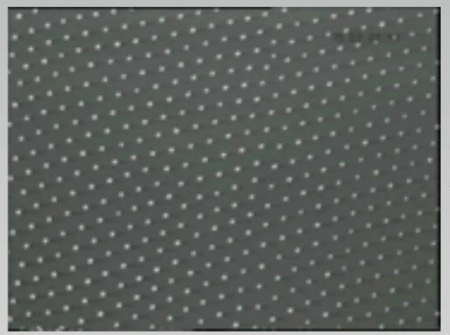
Key physics: Coupling Parameter - Γ controls self-organization

- Γ (coupling parameter) is indicative of the self-organizing, emergent properties of dusty plasmas.
- A dusty plasma can be used as a model system to investigate problems in soft-matter physics.
- Assume dust particles interact via a screened Coulomb interaction (Yukawa, Debye-Hückel):

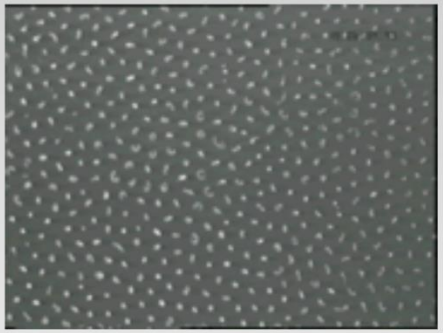
$$\varphi \sim \frac{\exp\left(-r/\lambda_D\right)}{r}$$

$$\Gamma = \frac{\text{electrostatic potential energy}}{\text{thermal energy}} = \frac{Q_d^2}{4\pi\varepsilon_0 k T_d \Delta}$$

$$\Delta = \text{Wigner-Seitz radius} = \left(\frac{4\pi n_d}{3}\right)^{-1/3}$$



$\Gamma >> 1$



$\Gamma \sim 1$

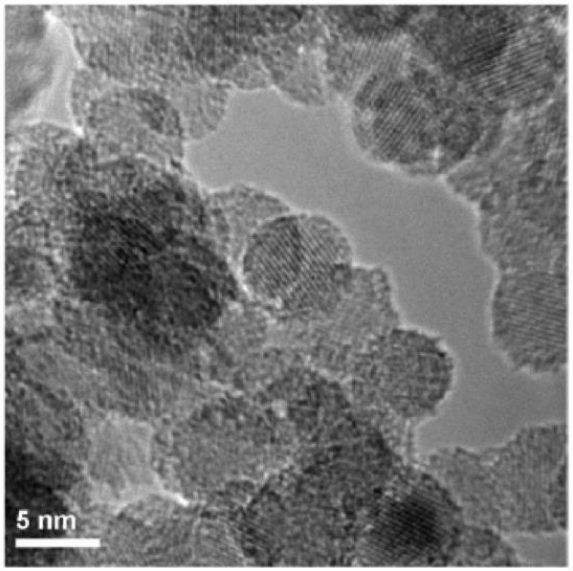
$\Gamma < 1$

- **Typical particle sizes: many to tens microns**
  Q_d = 1000's to 10,000s q

Ed Thomas, Auburn University

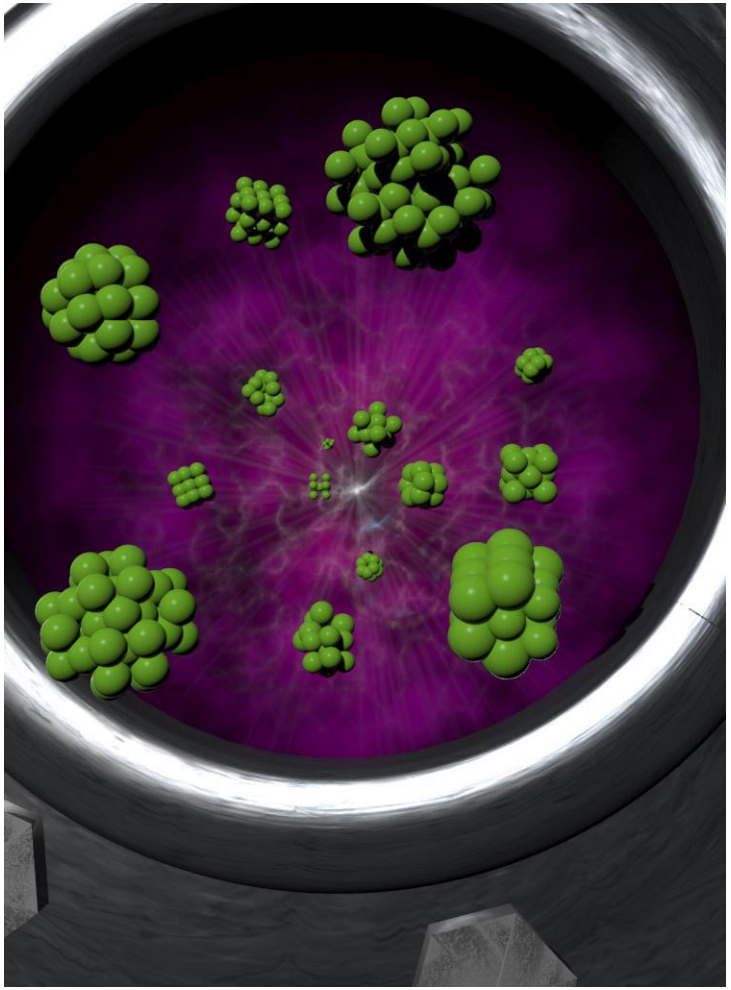
NANODUSTY PLASMAS (NDPs)

- Multiphase plasmas containing high density of nano-particles (< a few nm) that substantially affect plasma properties
- Most negative charge is on particles.
- Closely related to Macro-Dusty Plasmas with exceptions
  - Smaller particles that nucleate and grow.
  - Plasmas are chemically reactive
  - Particles are “active” in electrically and chemically perturbing plasma beyond charging.
  - Technologically important for materials synthesis.



- Silicon nanocrystals

NDPs: A GROWING FIELD



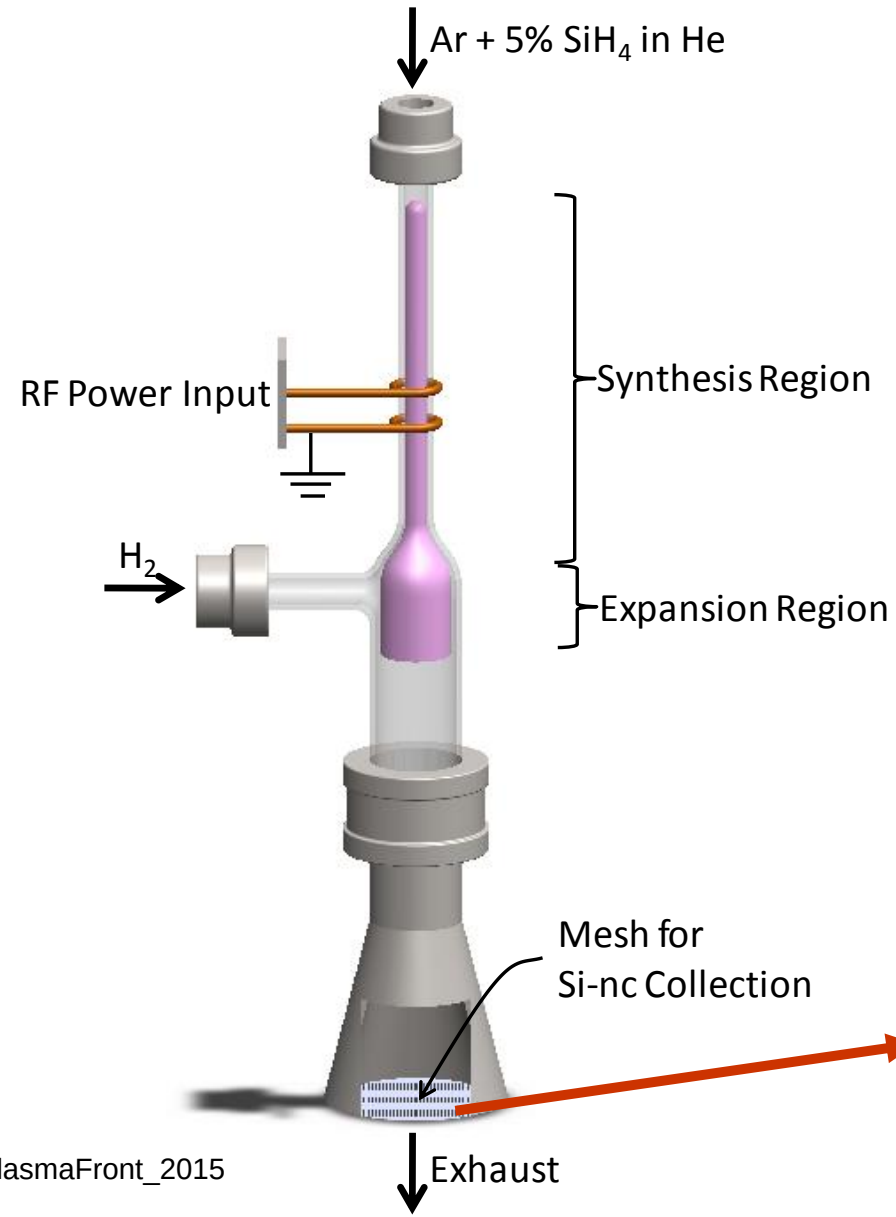
- **Due to importance of nano-particles in materials synthesis, growing interest in production of nanocrystals in low temperature plasma.**

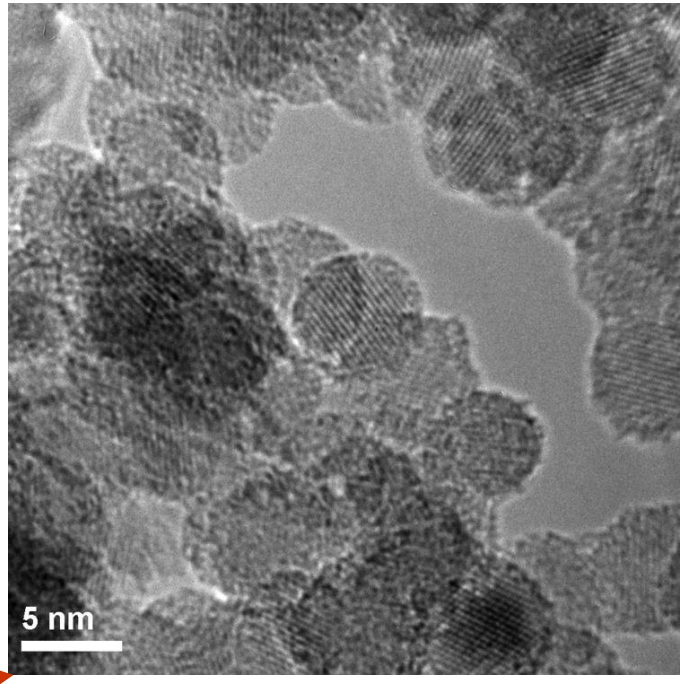
- **Special Issue of J. Phys. D: Appl. Phys. "Nonthermal plasma synthesis of nanoparticles"**
  Guest editors: M. Sankaran and U. Kortshagen
  Online publication: July 2015

- ***The technological applications have outstripped out fundamental understanding of these systems.***

MOTIVATION: PLASMA NANOCRYSTAL SYNTHESIS

- **Standard conditions:**
  - **10 sccm SiH_4:He (5:95)**
  - **50-100 sccm Ar**
  - **1-5 sccm H_2**
  - **200 Pa**
  - **5-10 W @ 13.56 MHz**
  - **~ 2-5 ms residence time**





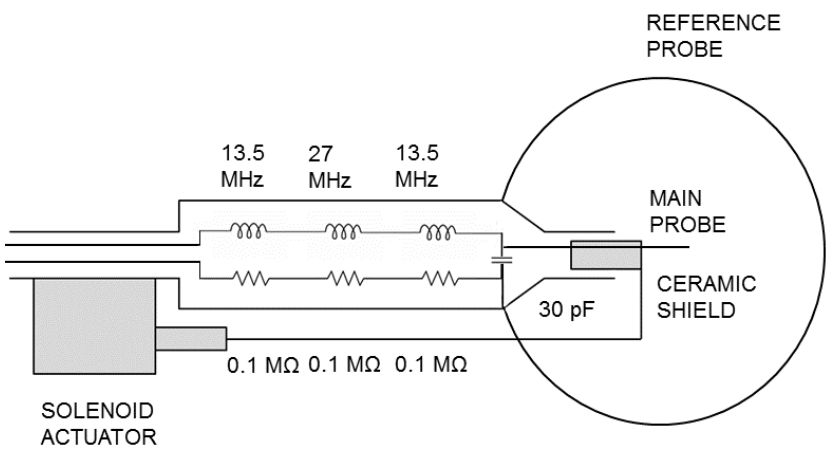
L. Mangolini et al., Nano Letters (2005)

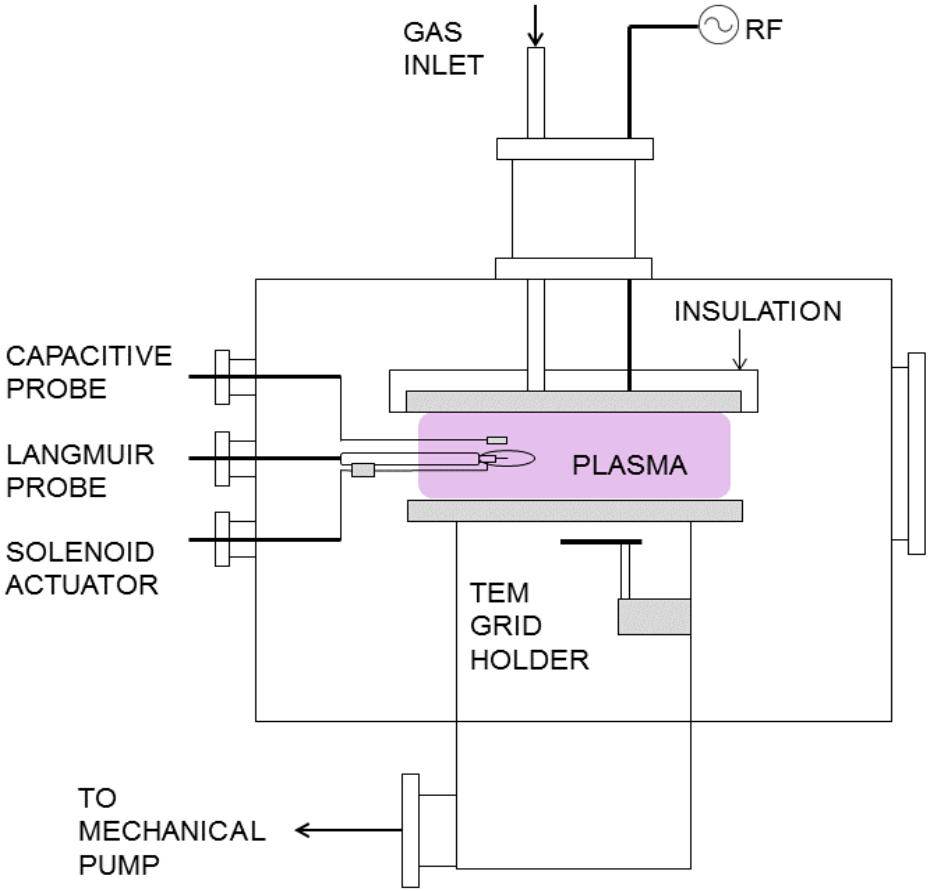
PLASMA PHYSICS CHALLENGES: THE PLASMA VIEWPOINT

- **Nanoparticles interspersed within plasma and small enough to be subject to statistical fluctuations.**
- **Nanoparticle densities 10^8 – 10^{11} cm^{-3} .**
- **The next solid phase surface is always less then one Debye length away.**
- **Traditional separation into bulk plasma / sheath / surface available to macro-dusty plasmas fails.**
- **Electron emission at nanoparticle surfaces will intrinsically (from within) affect the plasma properties.**
- **The particle size, chemical composition and mechanisms for feedback to plasma change over time.**
- **Feedback to fundamental properties of plasma – electrically, chemically.**

LANGMUIR PROBE MEASUREMENTS OF ELECTRON ENERGY DISTRIBUTION

- **Extremely challenging plasma environment for making fundamental measurements – particle contamination.**
- **Mechanically shielded Langmuir probe.**

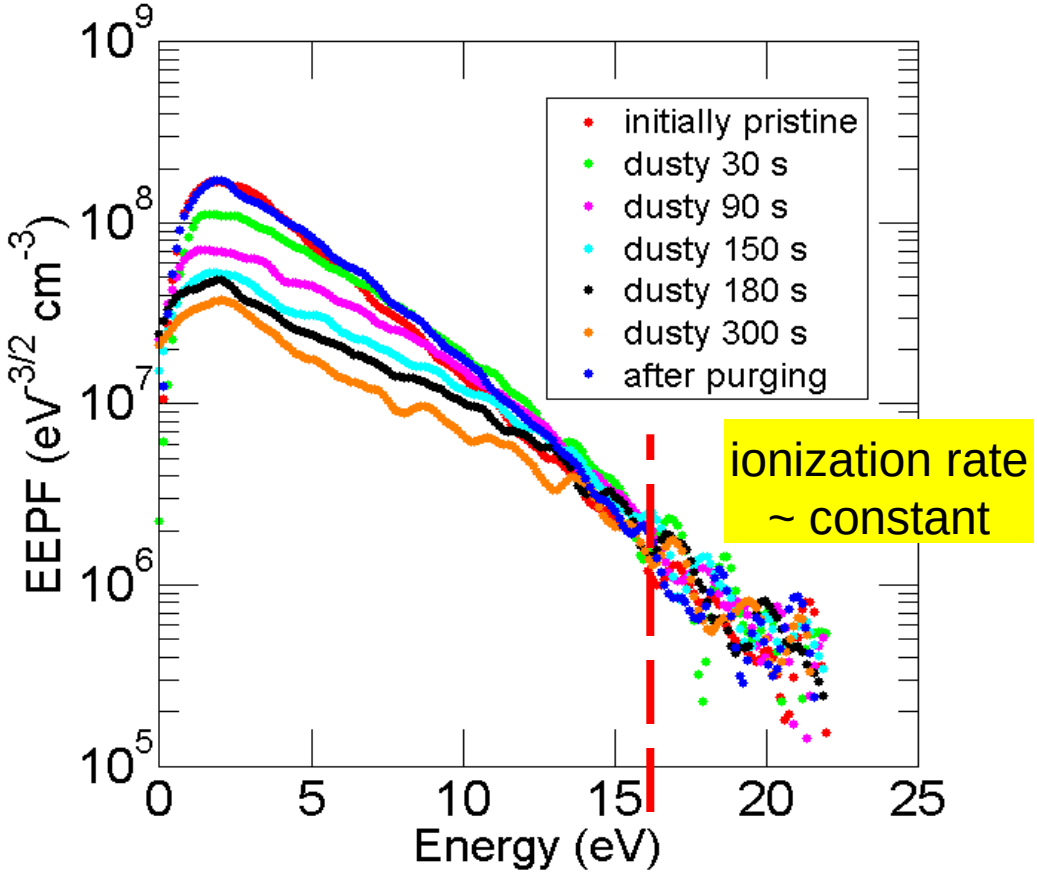




N. Bilik, Eet al., J. Phys. D: Appl. Phys. **48** (2015) 105204

TEMPORAL EVOLUTION OF EEPF IN DUSTY PLASMA

- **As particles grow, more negative charge resides on particles.**
- **Low energy portion of f(ε) depleted.**
- **Plasma must be sustained by ionization by high energy portion of f(ε) – less affected by particle growth.**



N. Bilik, Eet al., J. Phys. D: Appl. Phys. **48** (2015) 105204

EXAMPLE: NANOPARTICLE "INTERNAL" SURFACE AFFECTING PLASMA PROPERTIES

- **Particles interact with plasma through secondary electron emission and UV photodetachment.**
- **Feedback to plasma changes rate of growth of particles and particle density.**
- **Kortshagen and Bhandarkar, Phys Rev. E 60, 887 (1999)**

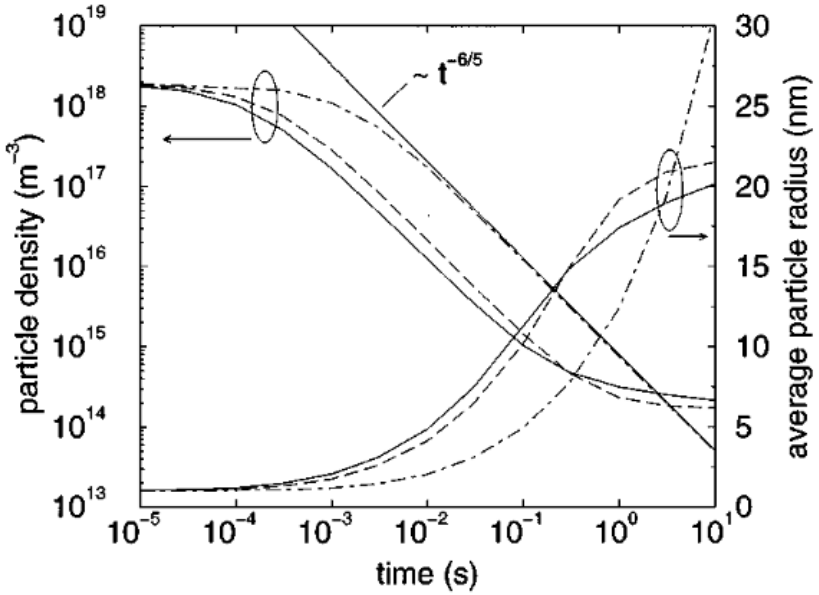


FIG. 2. Particle number density and average radius during coagulation. The full lines denote full UVPD and SEE ($Q=1$, $\gamma_i=0.4$, $\delta=3.5$), the dashed lines reduced UVPD and no SEE ($Q=0.25$, $\gamma_i=0$). The dash-dotted lines show the behavior of a neutral aerosol.

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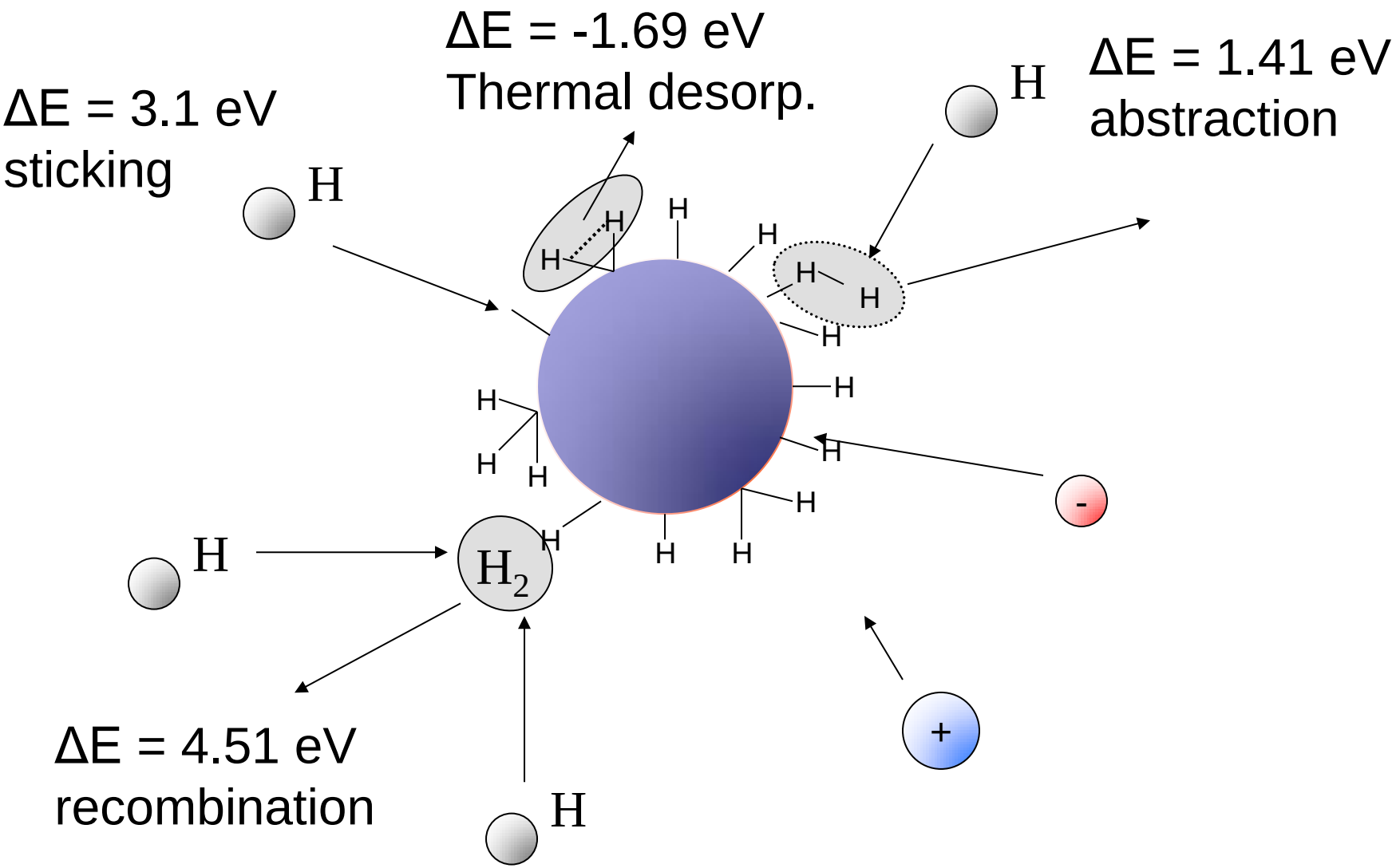
PLASMA PHYSICS CHALLENGES: THE NANOPARTICLE VIEWPOINT

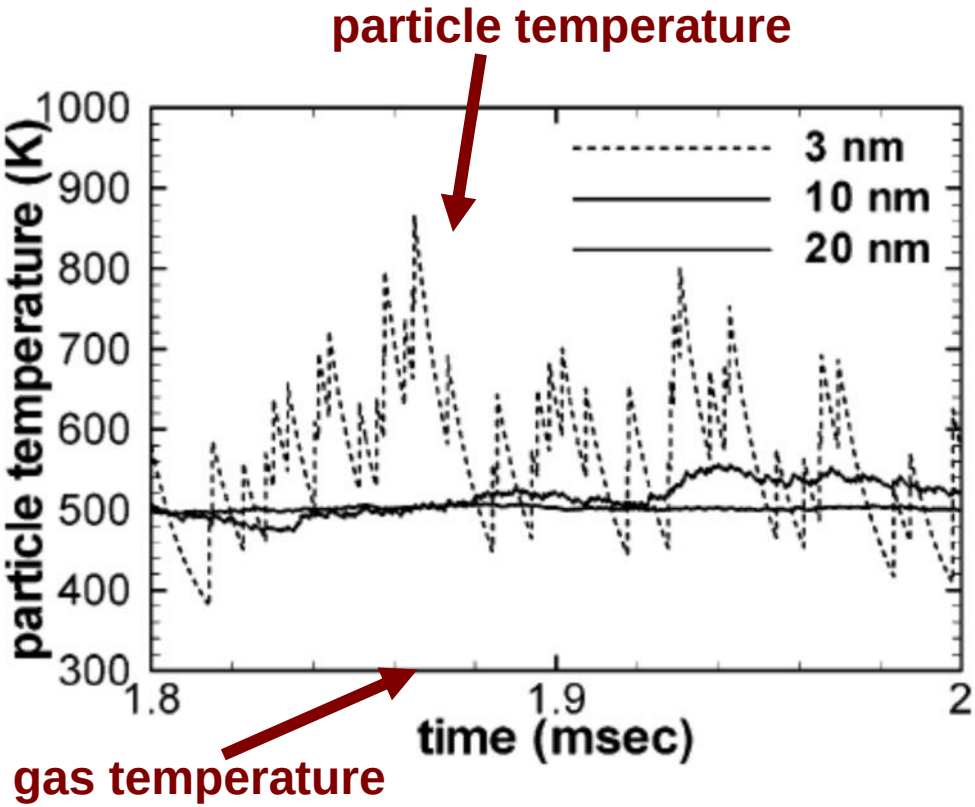
- **Energetic reactions on nanoparticle surfaces produce non-equilibrium between the nanoparticle temperature and the neutral gas temperature.**
- **Temperature of particles then feed back to plasma through enhanced thermal emission, difference reactivity with plasma produced radicals.**
- ***Plasma power is preferentially channeled into a sub-phase of the charged particles in a statistically stochastic fashion.***

NANOCRYSTAL HEATING


ΔE = -1.69 eV
Thermal desorp.
ΔE = 1.41 eV
abstraction
ΔE = 3.1 eV
sticking
H
H
H

STATISTICAL FLUCTUATIONS IN NANOPARTICLE TEMPERATURE

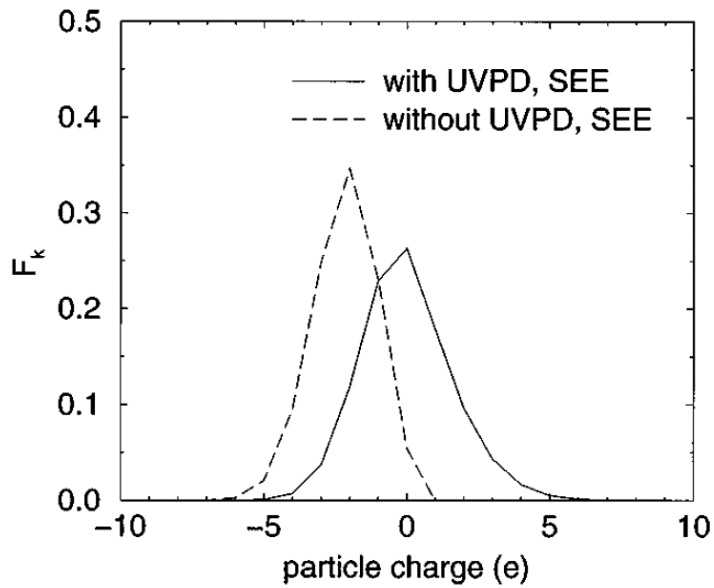
- **Nanoparticles are small!!**
- **Reactions of only a few radicals or ions are able to produced ΔT to an individual nanoparticle.**
- **Temperature fluctuations affect interaction of nanoparticles with plasma.**
- ***Intrinsically a stochastic system.***



L. Mangolini et al., Nano Letters (2005)

STATISTICAL FLUCTUATIONS IN NANOPARTICLE CHARGE

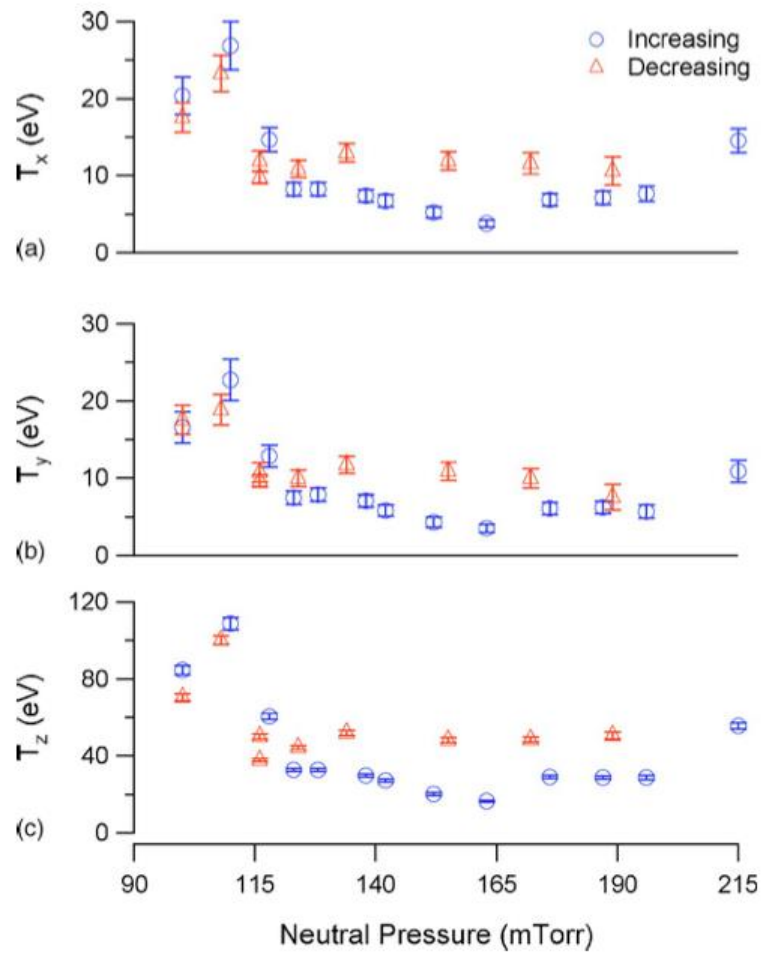
- **Nanoparticles are small!!**
- **On the average, even nanoparticles act as electrically floating bodies.**
- **However, their small size (only a few charges) results in particles statistically and significantly changing their charge – sometimes positive to negative.**
- ***Intrinsically a stochastic system.***



Particle charge distribution for $T_e = 4.2$ eV, $n_e = 2.45 \times 10^8$ cm^{-3}, and $n_i = 3.5 \times 10^9$ cm^{-3}. The full curve denotes the charge distribution with UVPD and SEE ($Q = 1$, $\gamma_i = 0.4$, $\delta = 3.5$), the dashed curve without these processes ($Q = 0$, $\gamma_i = 0$).

PLASMA PHYSICS CHALLENGES: MICROSCOPIC VIEW

- **High kinetic temperatures are observed in macro-dusty plasmas (micron-sized particles).**
- **These macro-dusty plasmas are more "discrete" than "fluid"(?).**
- **Nano-dusty plasmas having larger density of smaller particles are more "fluid" than "discrete"(?).**
- **Similar physical phenomena likely occur – with outlying particles in f(v) with high velocities.**
- ***How does this stochastic perturbation of velocity distribution of nanoparticle quasi-fluid affect plasma dynamics?***

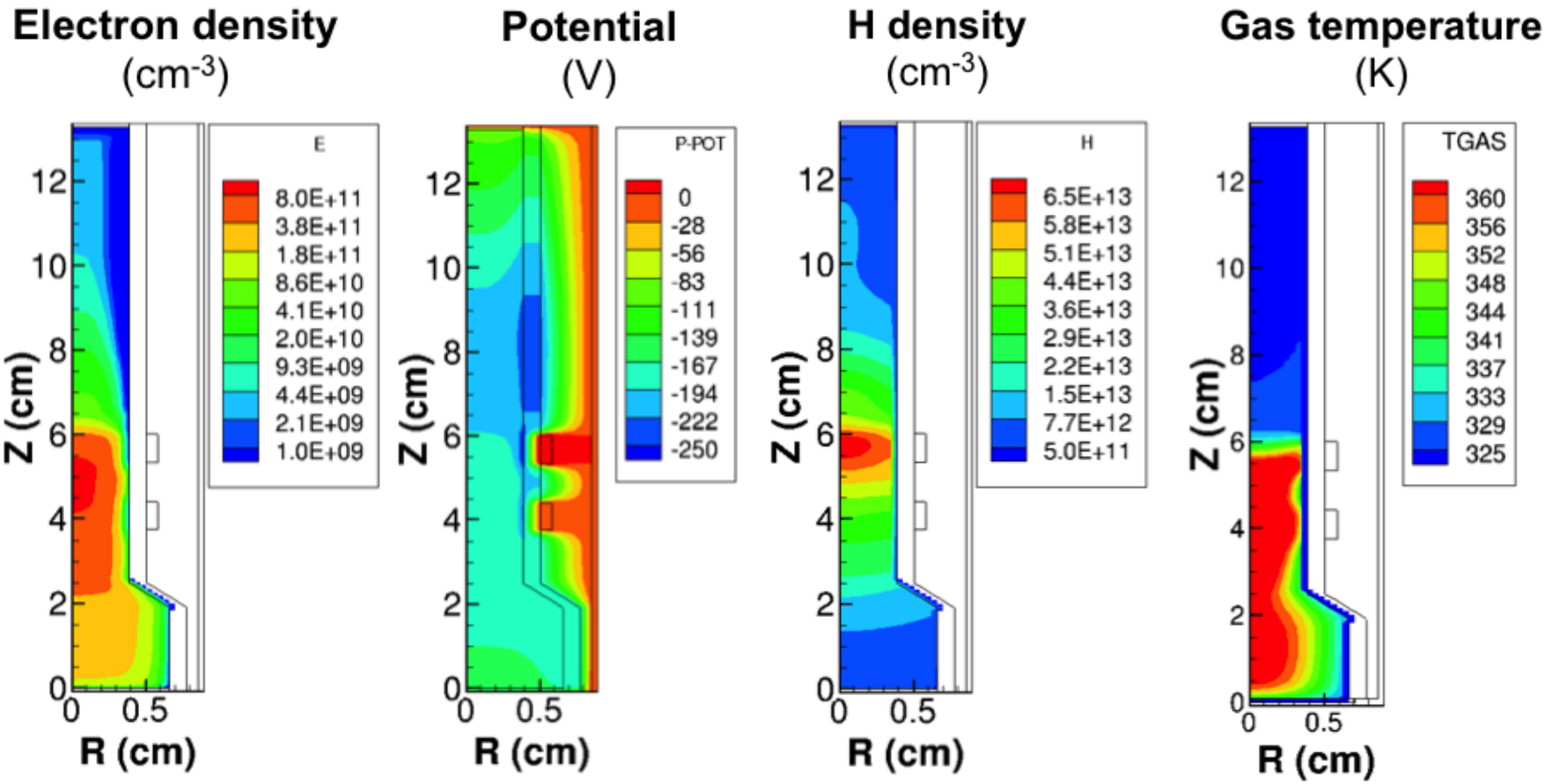


Example of high kinetic temperatures of 1.5μm particles in dusty plasma (Williams and Thomas, Phys. Plasmas **14**, 063702 (2007))

PLASMA-CHEMICAL HIERARCHY

- **Many traditional plasma studies treat electrons, ions, neutral, and discrete, well defined particles.**
- **NDPs are chemically reactive plasmas with 10s to 100s of chemical species and 1000s of possible plasma chemical reactions which grow the particles.**
- **Nano-particles have both a size and charge distribution, stochastically varying, requiring multi-fluid treatment of nanoparticle species.**
- **Nanoparticle nucleation is far from understood even for the most studied systems**

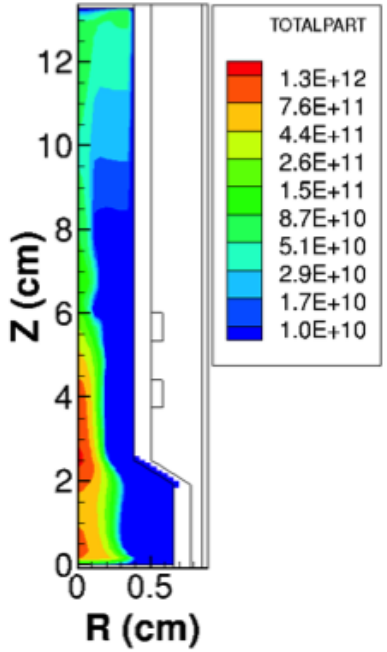
EXAMPLE: NUMERICAL SIMULATIONS OF CYLINDRICALLY FLOWING PLASMA



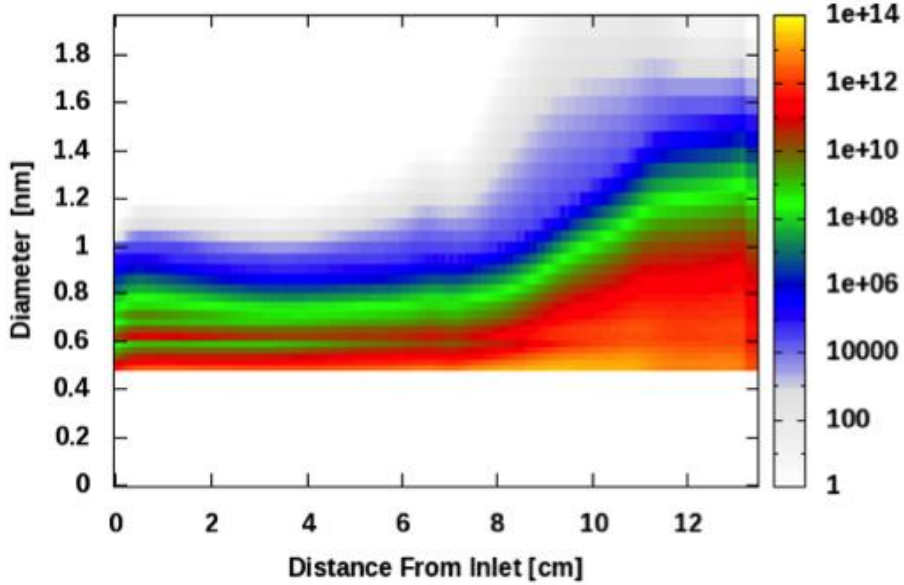
- **Self-consistent 2D model of plasma hydrodynamics model with aerosol sectional model for particle charging and interaction with bulk fluid.**
- **Ref: S. Girshick, U. Minnesota**

EXAMPLE: NUMERICAL SIMULATIONS OF CYLINDRICALLY FLOWING PLASMA

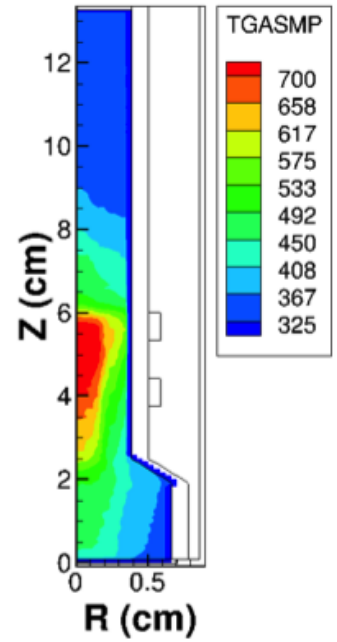
Total nanoparticle density (cm-3)



Particle size distribution on centerline



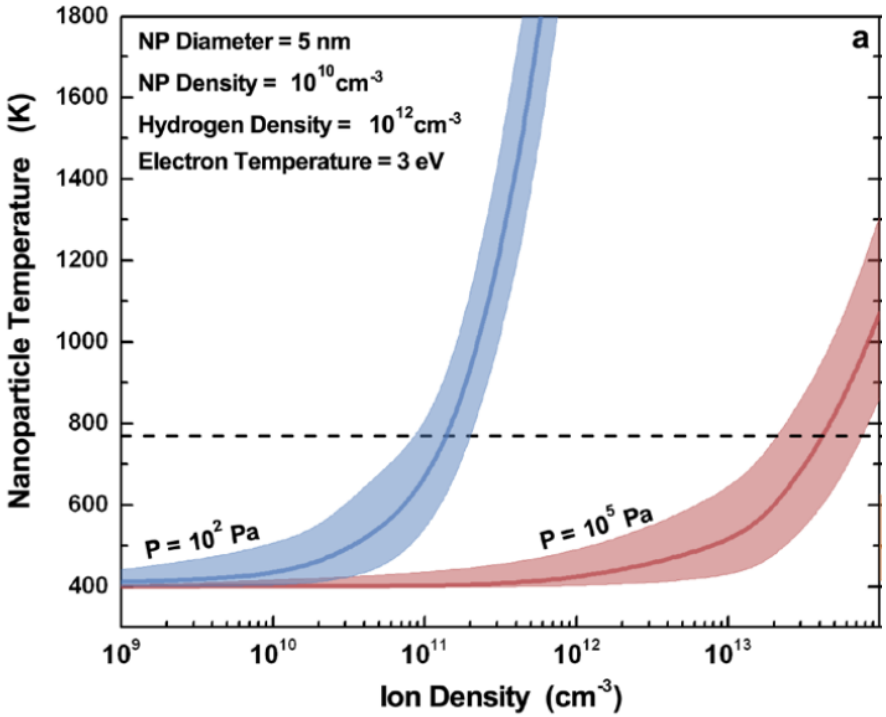
Internal temperature of 2-nm particles (K)



- **Monte Carlo model of nanoparticle heating based on local plasma properties**
- **First nanoparticle temperature calculations based on spatially varying plasma properties**

PLASMA PHYSICS CHALLENGES: MOVING TO ATMOSPHERIC PRESSURE

- **The vast majority of nanodusty plasma studies has focused on low pressure plasmas**
- **Atmospheric pressure becomes desirable for many practical applications**
- **First reports of nanodusty plasmas at atmospheric pressure already indicate strong difference, for instance in nanoparticle heating**



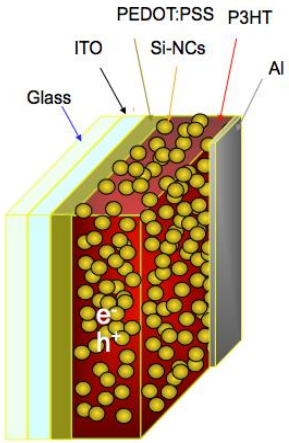
Comparison of nanoparticle heating at low pressure and atmospheric pressure (Aydil, Kortshagen et al., J. Phys. D.: Appl. Phys. **48** 035205 (2015))

SOCIETAL IMPACT

- **Nanodusty plasmas are a unique source of nanoparticles that cannot by generated with other approaches.**
- **Particularly useful for materials requiring high synthesis temperatures.**
- **Plasma produced nanocrystals may enable technological advances in fields including:**
  - **Renewable energy generation**
  - **Energy conversion**
  - **Energy storage**
  - **Biotechnology**
  - **Human medicine**
- **Enable scientific advances in materials science and solid state physics (e.g. study of metal-insulator transition in nanocrystal solids).**

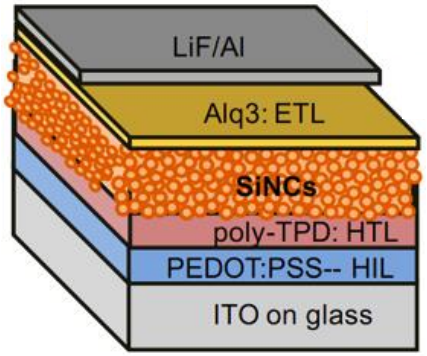
APPLICATIONS OF PLASMA-SYNTHESIZED NCS

Si NC PV cells



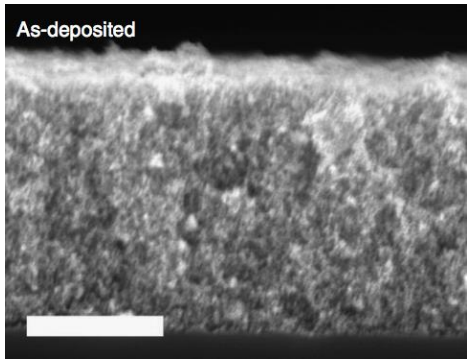
Kortshagen et al., Nano Letters 2009

Si NC LED, EQE>9%



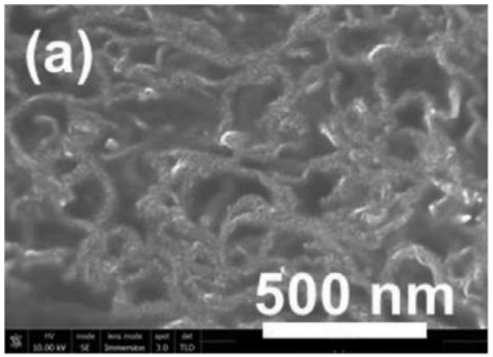
Kortshagen et al., Nano Letters 2010, 2011

ZnO films with high mobility



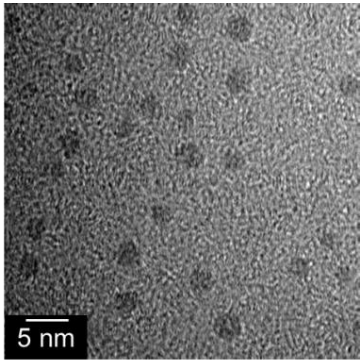
Thimsen, Aydil, Kortshagen et al., Nat. Comm. 2014

Si NC anodes for Li ion batteries



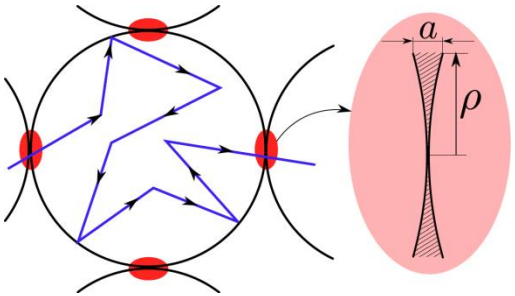
Mangolini et al., J. Power Sources 2015

Nucleation of nanodiamond



Sankaran et al., Nat. Comm. 2013

Metal-insulator transition in NC solids



Shklovskii, Kortshagen, et al., Nat. Mater., under review

RESEARCH FRONTIER CHALLENGES

- ***Understand how intrinsically stochastic nature of nano-dusty plasmas affects kinetic distributions (energy, velocity) of charged particles of a quasi-nano-fluid.***
- **A platform to test understanding of plasma surface interactions from *the inside of a plasma.***
- **A means of studying the *thermodynamics of multiphase plasmas.* What is the thermodynamic heat conduction and electrical conductivity of the *quasi-nano-fluid*?**
- **Strict test of thermodynamics.**
- **From a technological perspective, understand how plasma species affect nanoparticle properties.**

RESEARCH FRONTIER CHALLENGES

- **The "multi-fluid" character of nanodusty plasmas is maybe among the *more complex plasma problems,* requiring the development of new experimental and numerical tools for improved understanding**
- **Diagnostics do not now exist capable of resolving (imaging?) stochastic properties of plasma nano-particle interactions.**
- **Spatially resolved measurements of nanoparticle f(v) will provide insights the heating mechanisms and interactions that provide anomalously high particle velocities in *quasi-nano-fluids*.**
- **New computational algorithms required to address growth of nanoparticles (sizes, charge states) – applicable to other plasma-thermo-chemical systems.**

CONNECTIVITY WITH OTHER WHITEPAPERS

- **Paul Bellan – *Lab Experiments Relevant to Space, Solar and Astrophysical (SSA) plasmas.***
  - **Interaction of plasmas with ice-crystals. Source of agglomeration, formation of non-spherical agglomerates, feedback to properties of plasmas, polarization of radiation.**
- **Guradas Ganguli – *Plasma Turbulence in Nature and the Lab***
  - **"Consider a 3-species (ion, electron, and dust) plasma"**
  - **Are anomalous velocities of particles a consequence of localized turbulent processes?**
- **R. Paul Drake – *Nonequilibrium Approaches to Averaged Properties***
  - **Transport coefficients may differ from equilibrium values.**
  - **Phase changes – structured solid vs partially ionized molecular soup vs ionized gas.**
  - **Approaches to non-equilibrium models – multiscale, practical integrated models, non-equilibrium statistical mechanics?**

CONNECTIVITY WITH OTHER WHITEPAPERS

- **Matthew Kunz – *Magnetic Self Organization in Multi-Scale Astrophysical Plasmas.***
  - **Astrophysical *(nanodusty!!)* plasmas are multiscale phenomena whose behavior at the largest scales depends on the details of the smallest scale.**