Homogeneous nucleation experiment of cosmic dust

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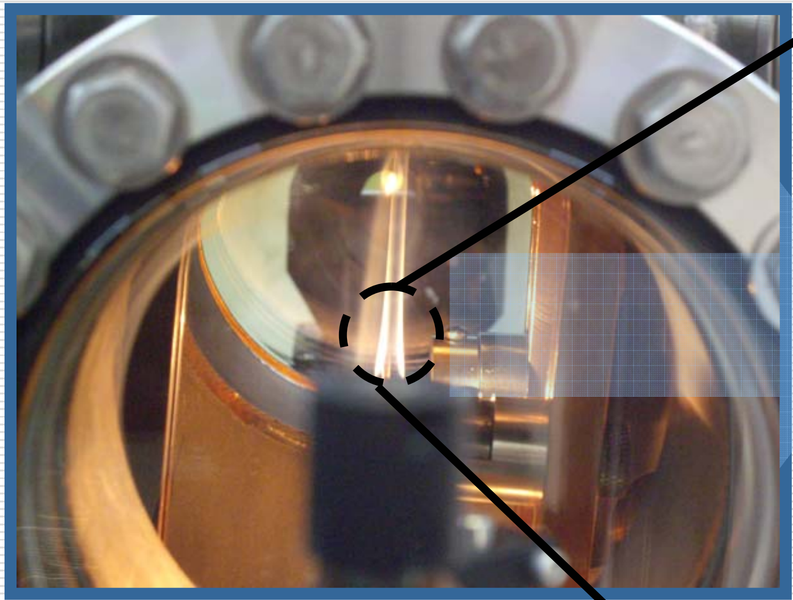
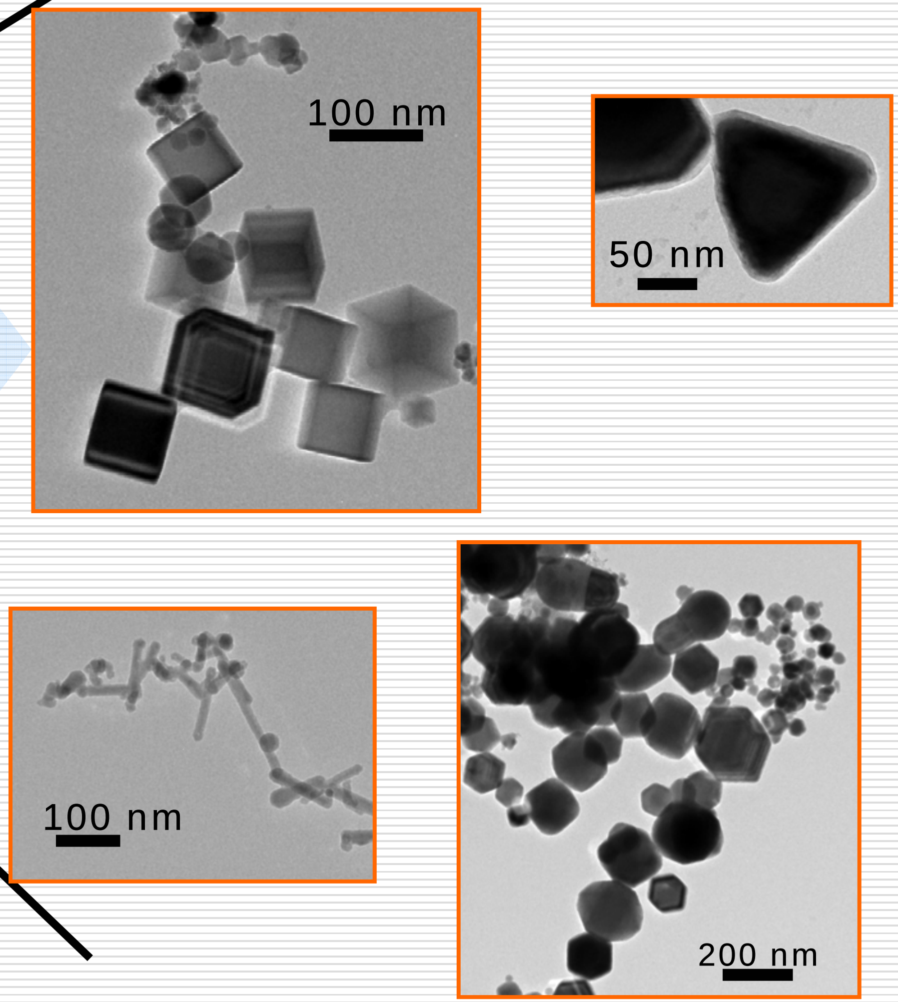
(93) GFW, 神戸 CPS, November 9th, 2011.

Nucleation in Lab & Space

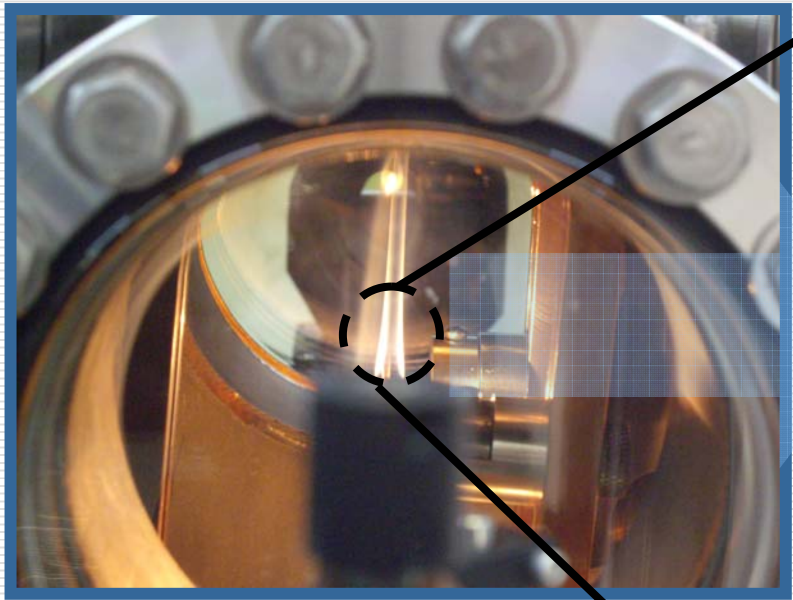


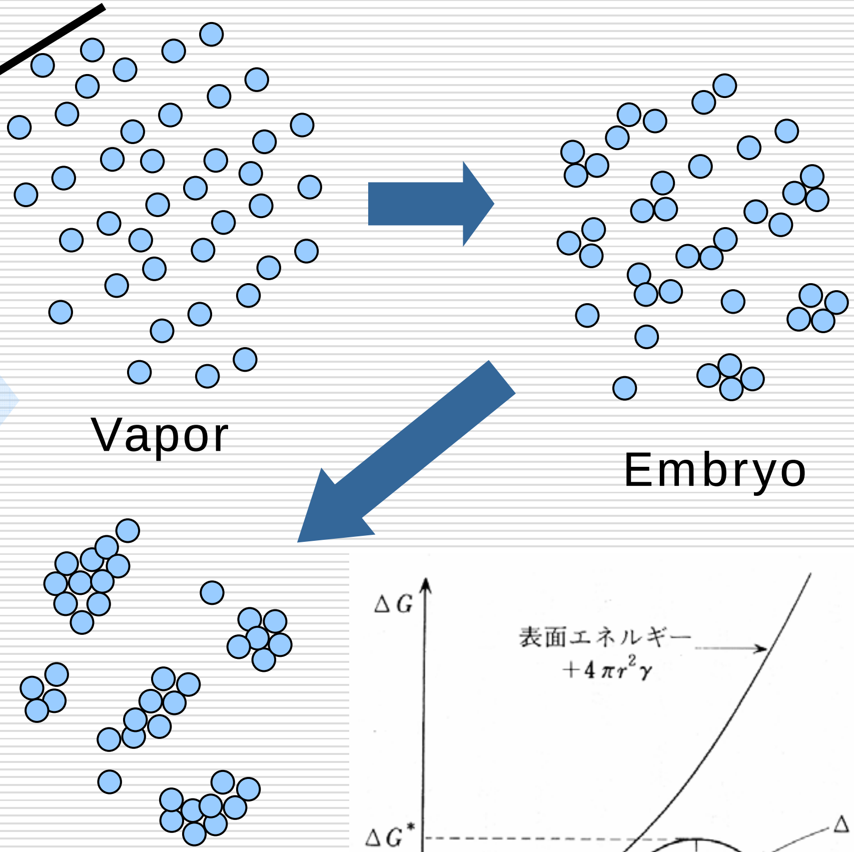


Why nucleation?

- Number
- Morphology
- Crystal habit
- Size
- Size distribution
- Polymorphism

Nucleation in Lab & Space





Why nucleation?

- Number
- Morphology
- Crystal habit
- Size
- Size distribution
- Polymorphism

黒田登志雄
結晶は生きている

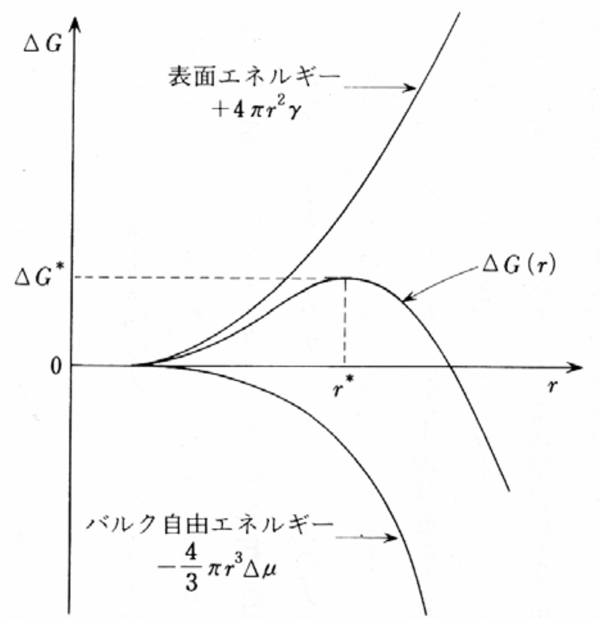
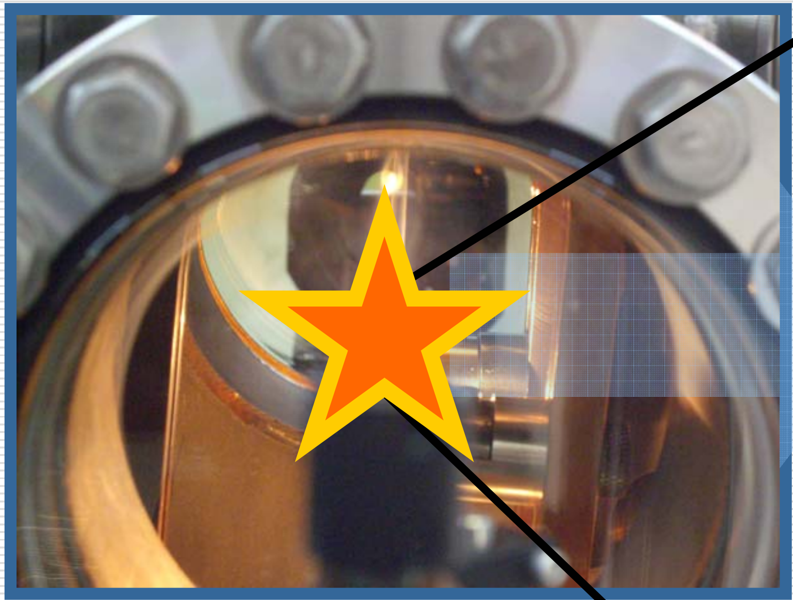
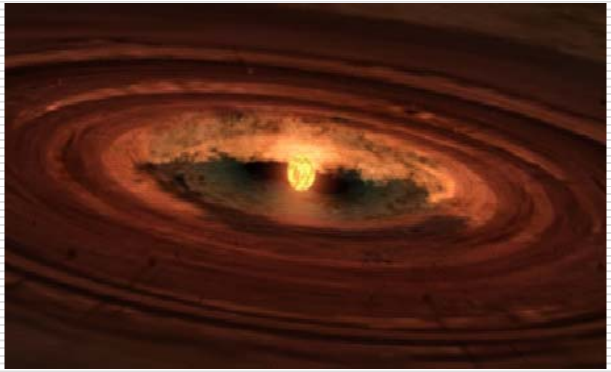


図 2.4　臨界核の半径 r^* と核生成に必要な自由エネルギー変化 ΔG^*.

Nucleation in Lab & Space



Evolved Star

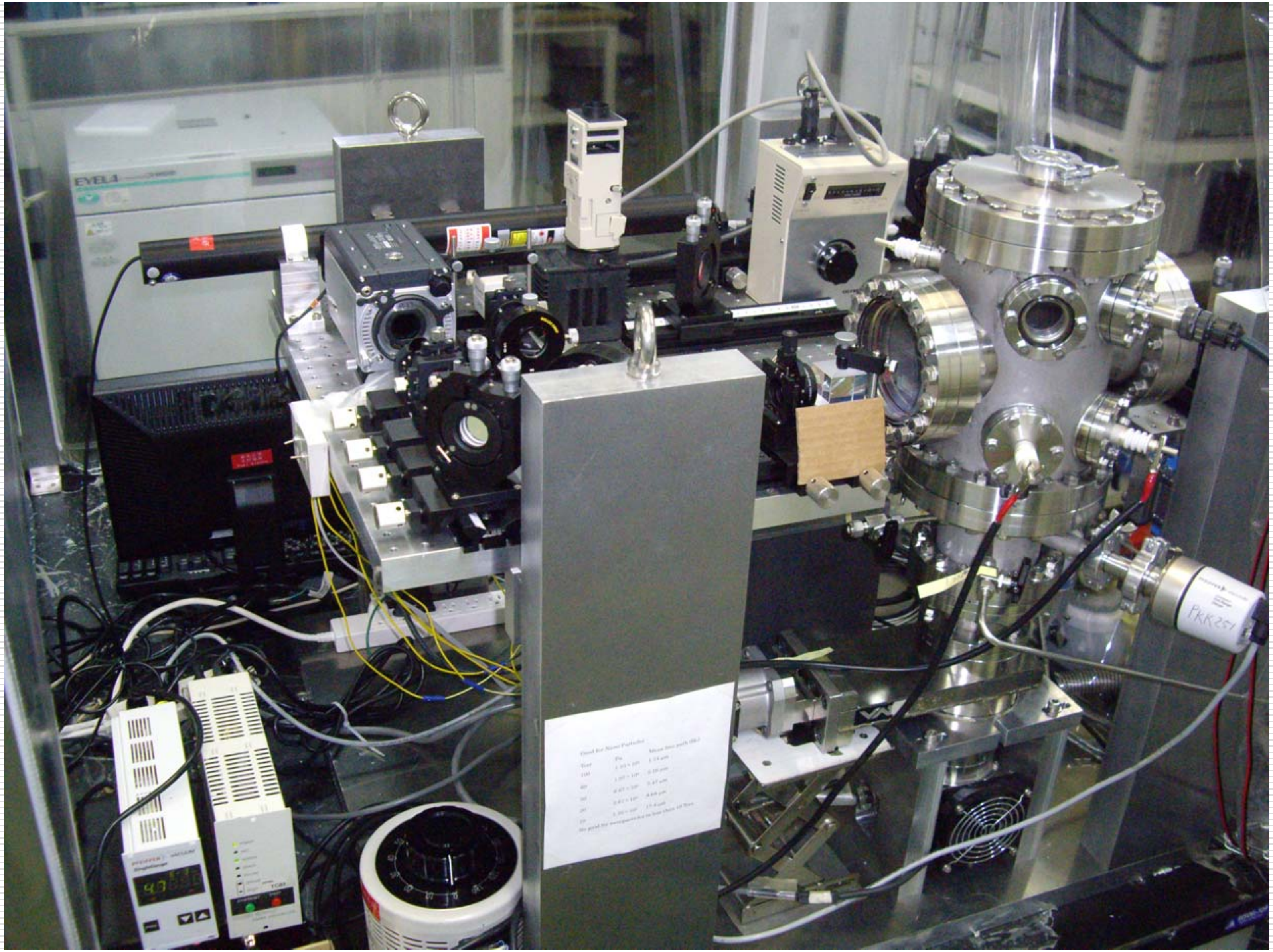


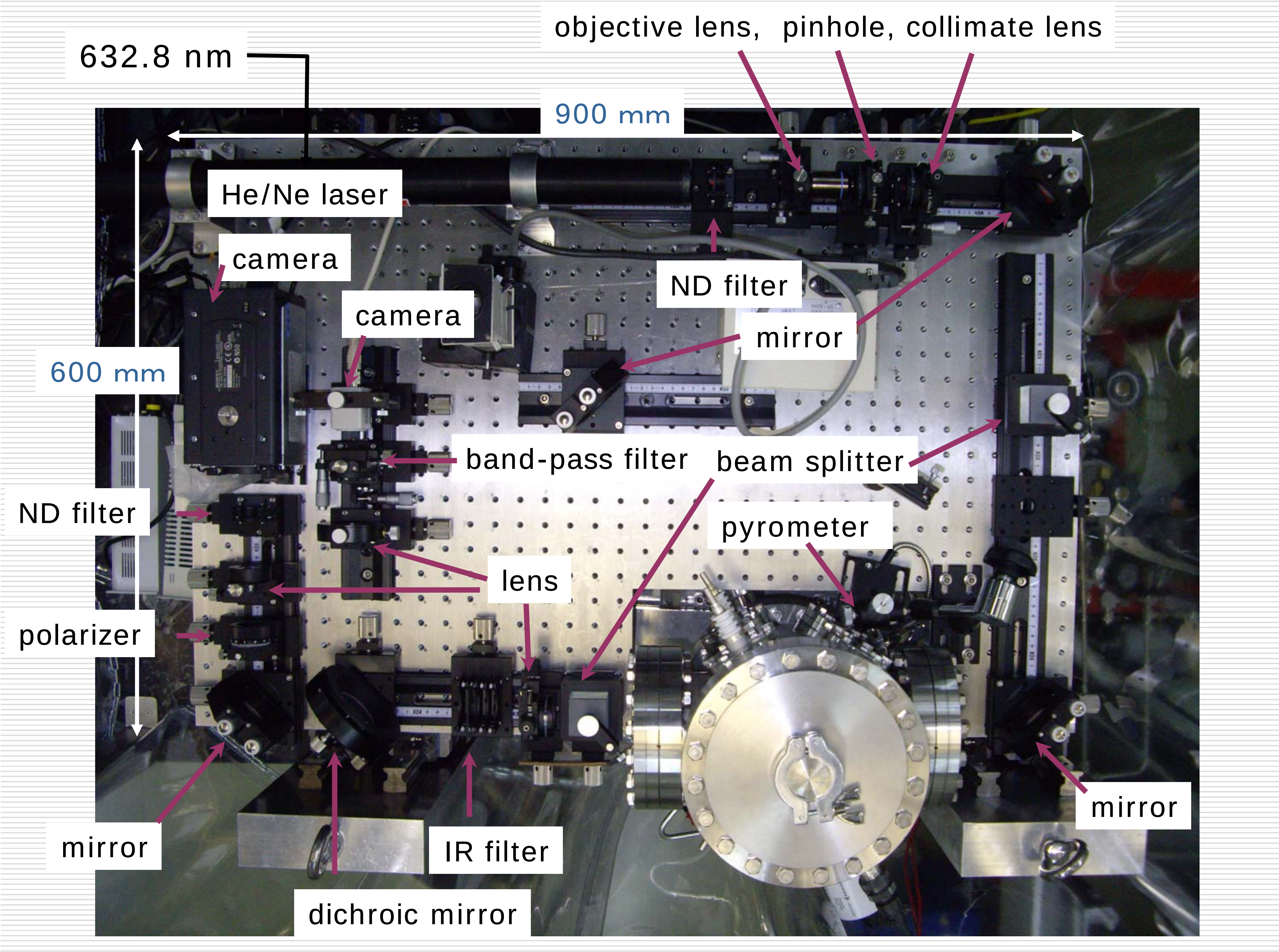
Planetary Nebula

Why nucleation?

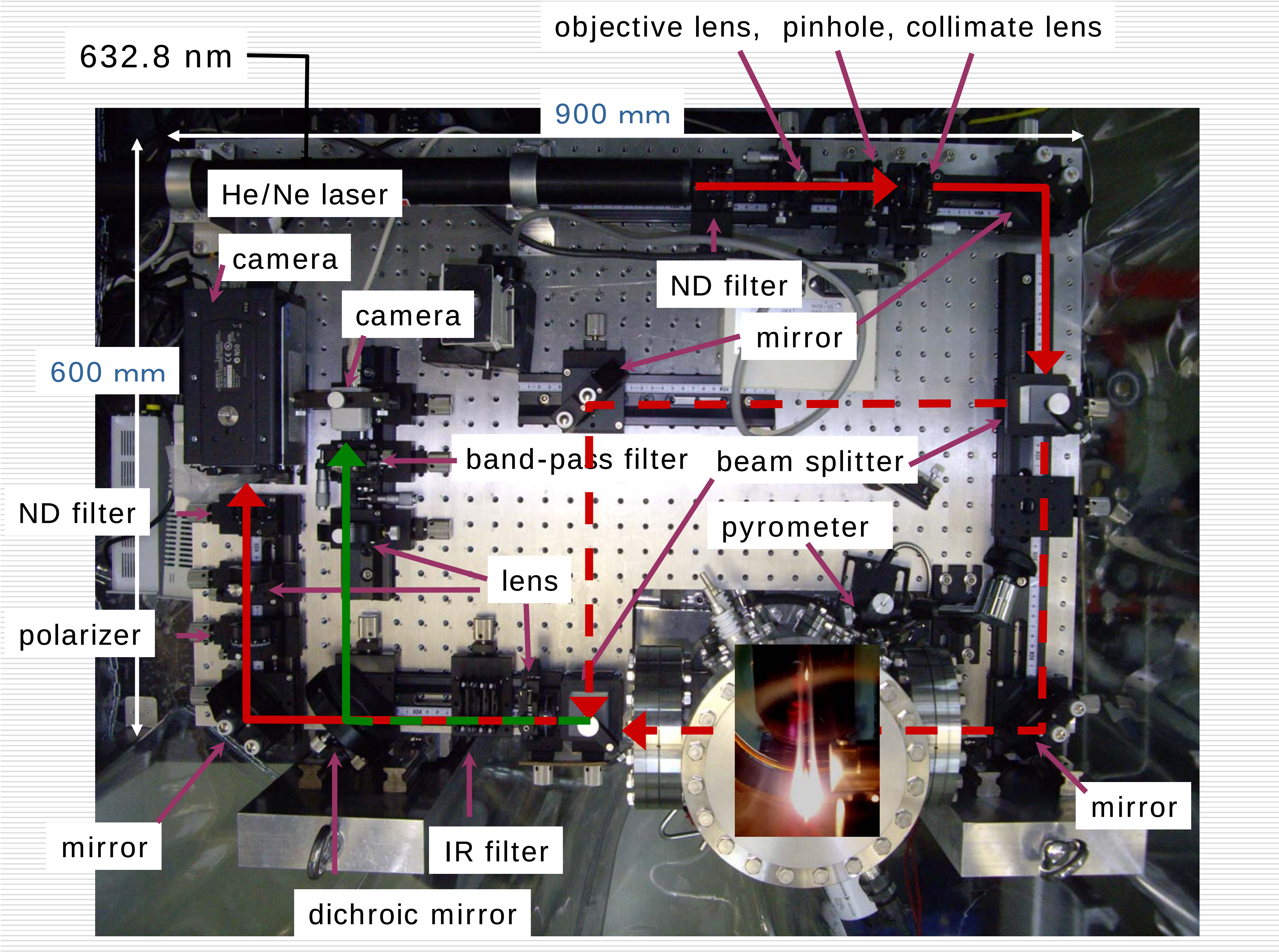
- Number
- Morphology
- Crystal habit
- Size
- Size distribution
- Polymorphism

Chamber and optics





632.8 nm
objective lens, pinhole, collimate lens
900 mm
He/Ne laser
camera
ND filter
camera
mirror
600 mm
band-pass filter
beam splitter
ND filter
pyrometer
lens
polarizer
mirror
mirror
IR filter
dichroic mirror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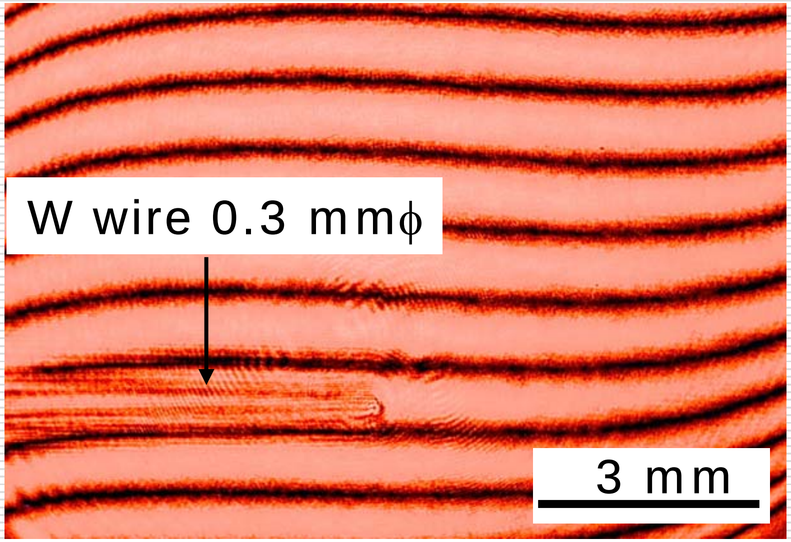
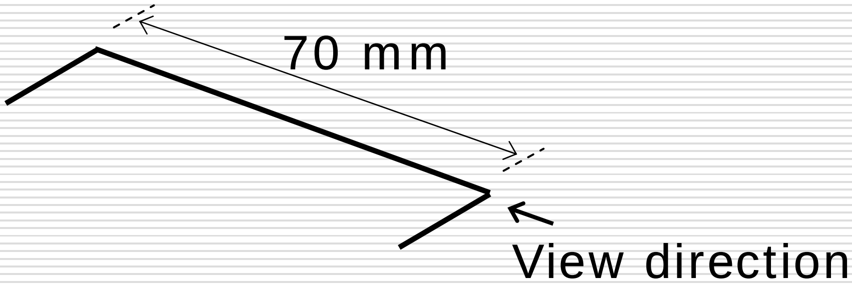
ND filter
pyrometer
lens
polarizer
mirror
mirror
IR filter
dichroic mirror

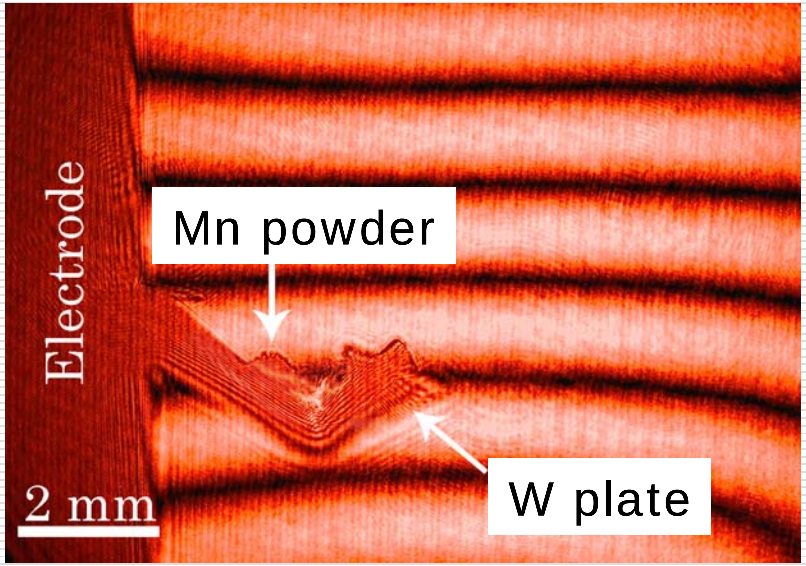
Interferogram

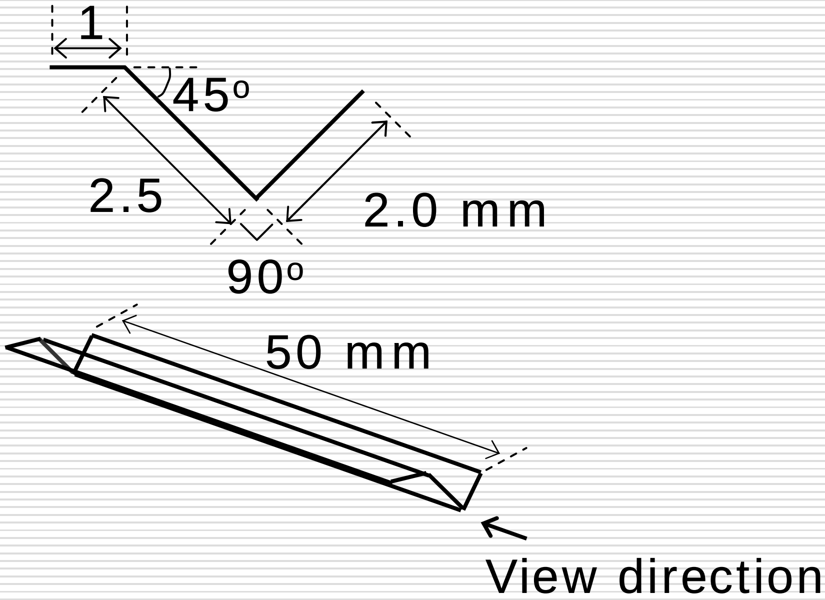
WO_3: Ar 9×10^3, O_2 1×10^3 Pa





Mn: Ar 2×10^4 Pa



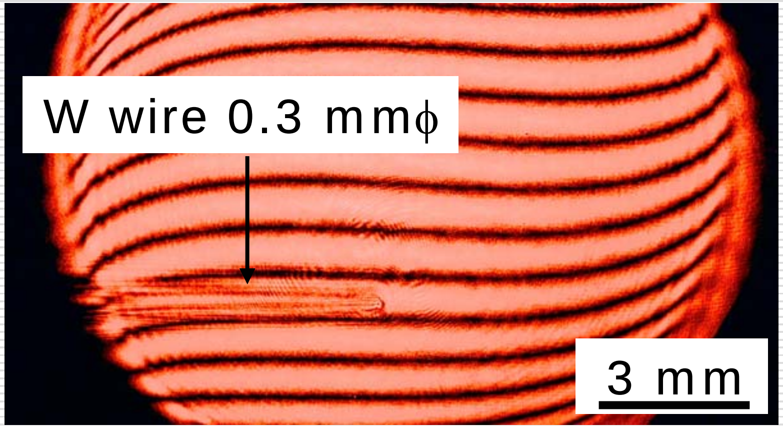


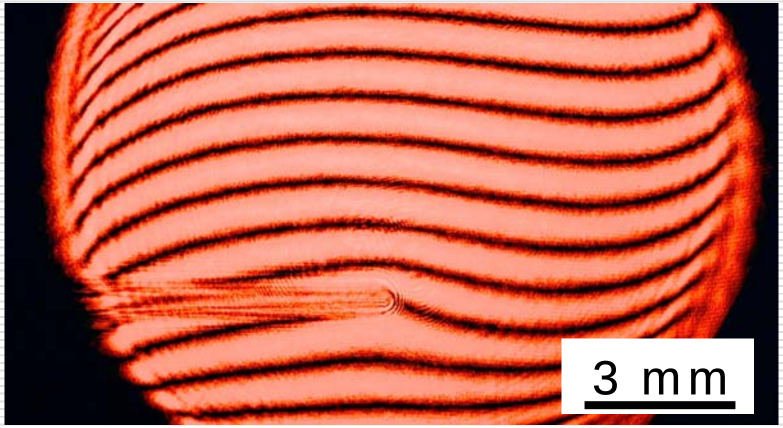
Interferogram

Temperature: 298 K (25^{o}C)
Gas: Ar 1×10^{4} Pa
Refractive index: 1.00002714

Heating

Temperature: 323 K (50^{o}C)
Gas: Ar 1×10^{4} Pa
Refractive index: 1.00002503





We can detect only a difference of 10^{-6}-10^{-7} orders!!

$$n_{Ar(T,P)} - 1 = \frac{[n_{Ar(273.15,P_0)} - 1]}{1 + a\Delta T} \frac{P}{P_0}$$

$$\Delta d = \{(n(T_0,P_0) - n(T,P)\} \times l / \lambda .$$

a: the coefficient of volume expansion,
Δd: degree of movement,

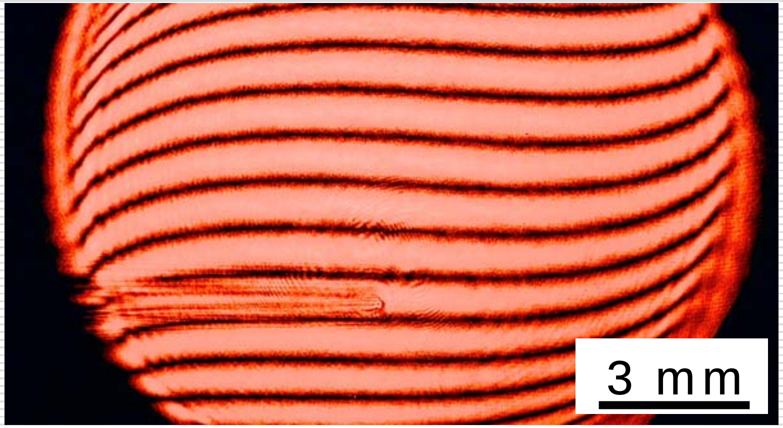
P_0: 101333.25 Pa
l: the physical length

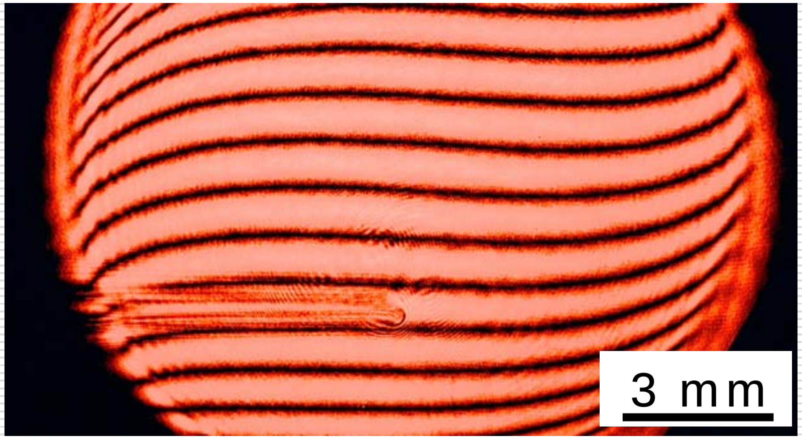
In-situ observation of nucleation: WO_3

Temperature: 298 K (25ºC)
Gas: Ar 1×10^4 Pa
Refractive index: 1.00002714

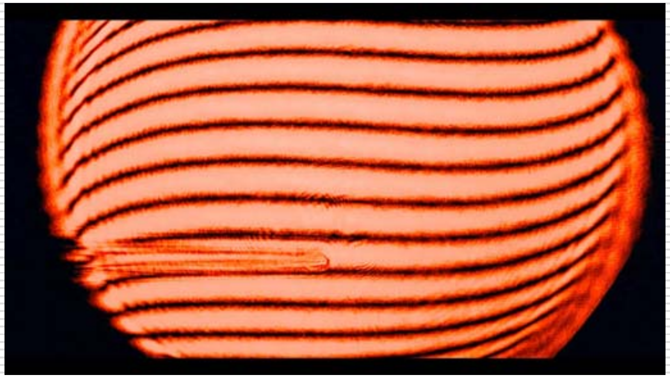
Oxygen →

Temperature : 298 K (25ºC)
Gas : Ar 9×10^3 Pa, O_2 1×10^3 Pa
Refractive index: 1.00002703





Heating
RT
↓
1570 K



Only Temperature

Temperature & concentration

Temperature information is subtracted by oxygen free experiment.

In-situ observation of nucleation: Mn

5 times fast

in Ar: 2.0×10^4 Pa

Evaporation Source

T: 1953 K

P_e: 1.6×10^4 Pa

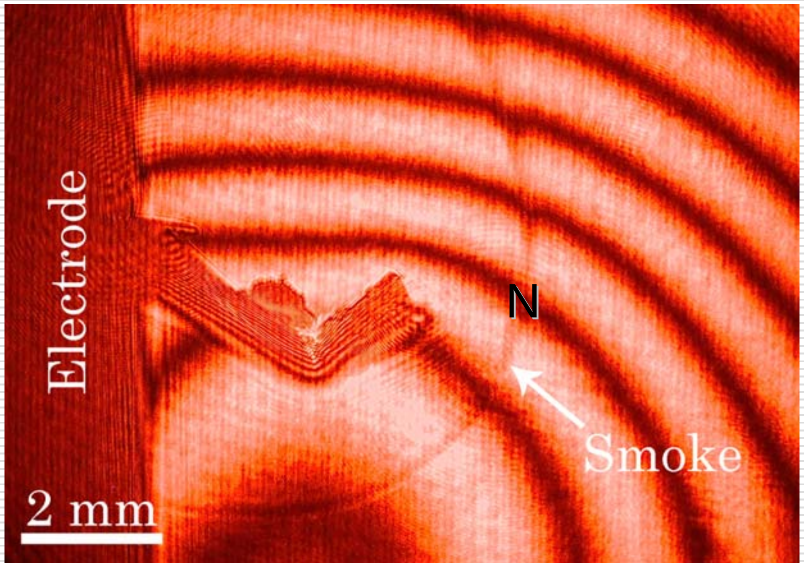
Nucleation site "N"

T: **1100 K**

P: 2.7×10^3 Pa

P_e: 4.4×10^{-2} Pa

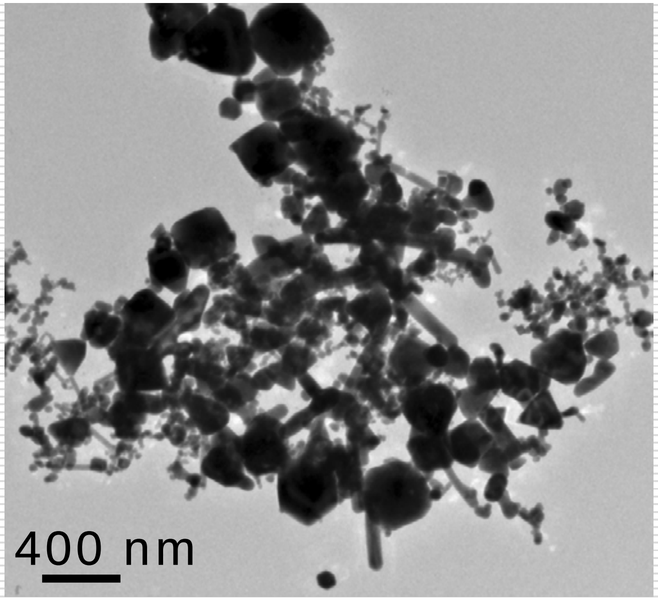
P/P_e = **6.1×10^4**

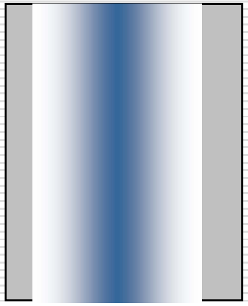


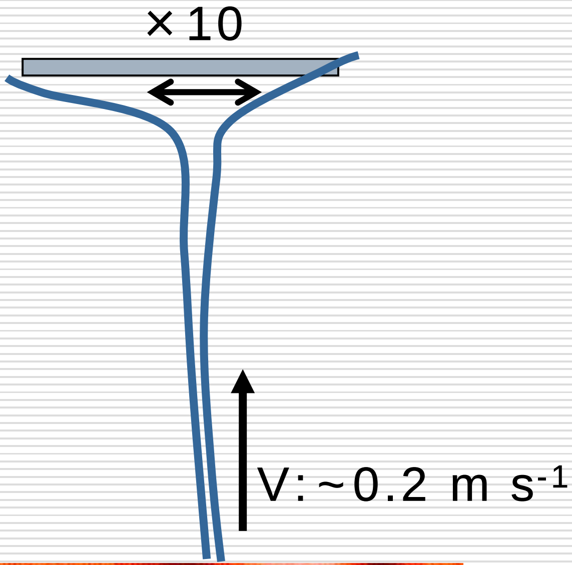
Condensation temperature (1100 K) is significantly lower than their equilibrium temperature (1760 K) at 2.7×10^3 Pa.

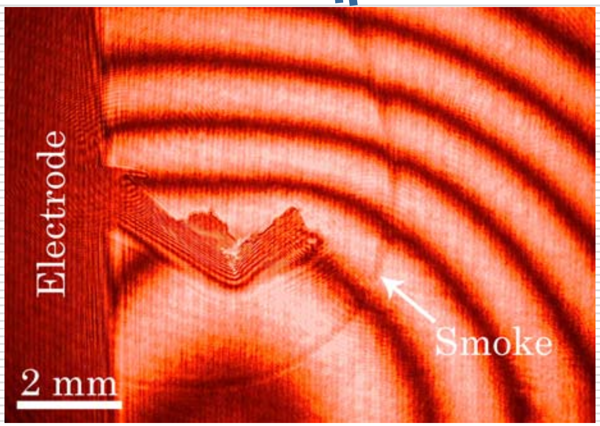
ΔT = 660 K

In-situ observation of nucleation: Mn









Mean radius: 13.7 nm

Number density: 6×10^{15} m^{-3}

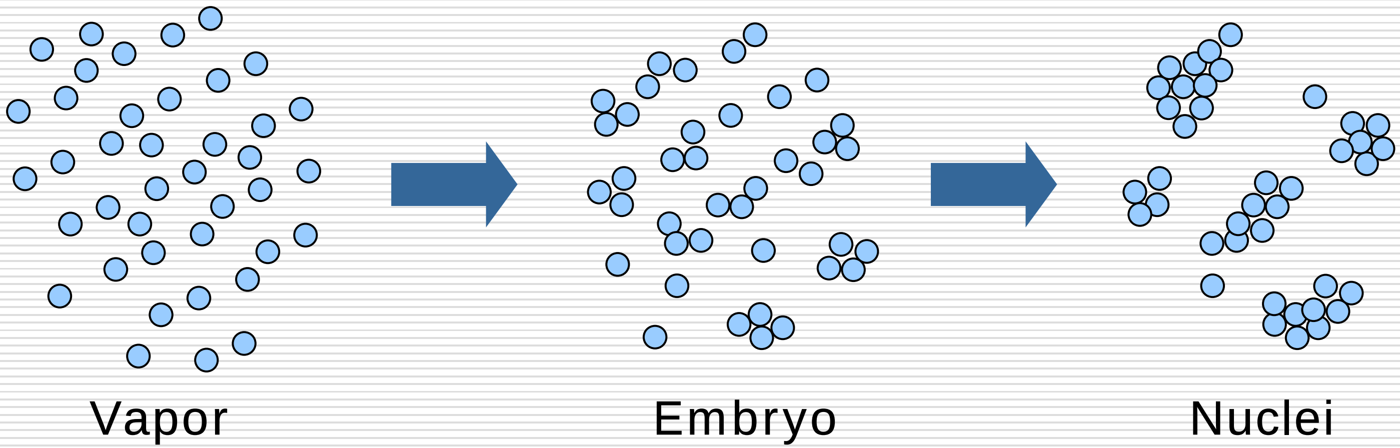
$= 10 \times \rho / (V \times t)$

ρ: Number density on the grid (m^{-2})
V: Velocity of smoke ($m\ s^{-1}$)
t: Experimental duration (s)

Is there useful nucleation theory?

Classical nucleation theory does not work in nano-scale.

Indeed, nucleation rate from classical theory is far from experimental (water, ethanol, etc) & MD simulation (water, inert gas) values. (Feder 1966、Schmitt et al. 1982, Adams et al.1984, Yasuoka et al. 1998, Toxvaerd 2001, 2003)



Must consider intermolecular interaction.

Is there useful nucleation theory?

Semi-phenomenological nucleation theory: SP

(Dillmann & Meier 1991)

$$\mu_i = kT\log(P_i/P_e) + i\mu_{solid} + \sigma \mathbf{A_1} i^{2/3} + \underline{+\mathbf{A_2}}\, i^{1/3} - \sigma A_1 \underline{-\mathbf{A_2}}$$

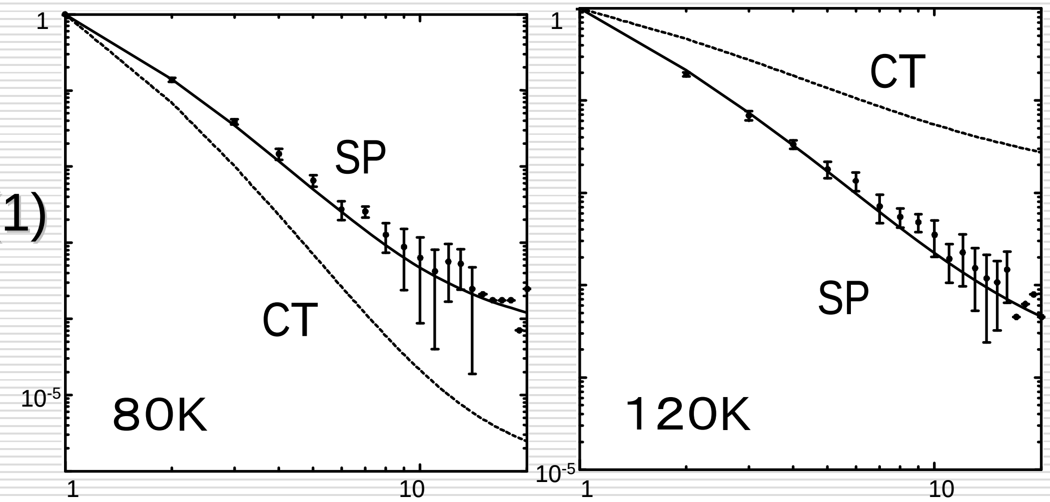
Correction term

Correction term: Determined by second virial coefficient.

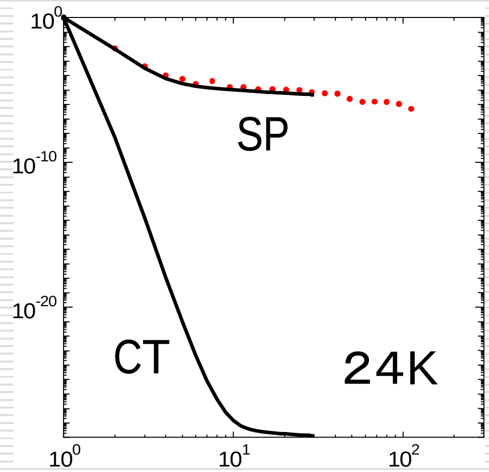
σ : Surface energy per unit area

MD calculation of Liquid (Tanaka et al. 2005)

n(i)/n(1)



MD calculation of Solid



(Tanaka et al. 2011)

Number of molecules in a cluster; i

Values for model calculation

- Initial pressure of Mn: $P_0 = 2.7 \times 10^3$ Pa
- Time scale for cooling: $\tau = 1.12 \times 10^{-3}$ s

Experiment

- Surface free energy of molten Mn at 1573-1773K: 1100 erg/cm^2

Physical Chemistry of High Temperature Technology, E.T. Turkdogan, Academic Press, New York, 1980

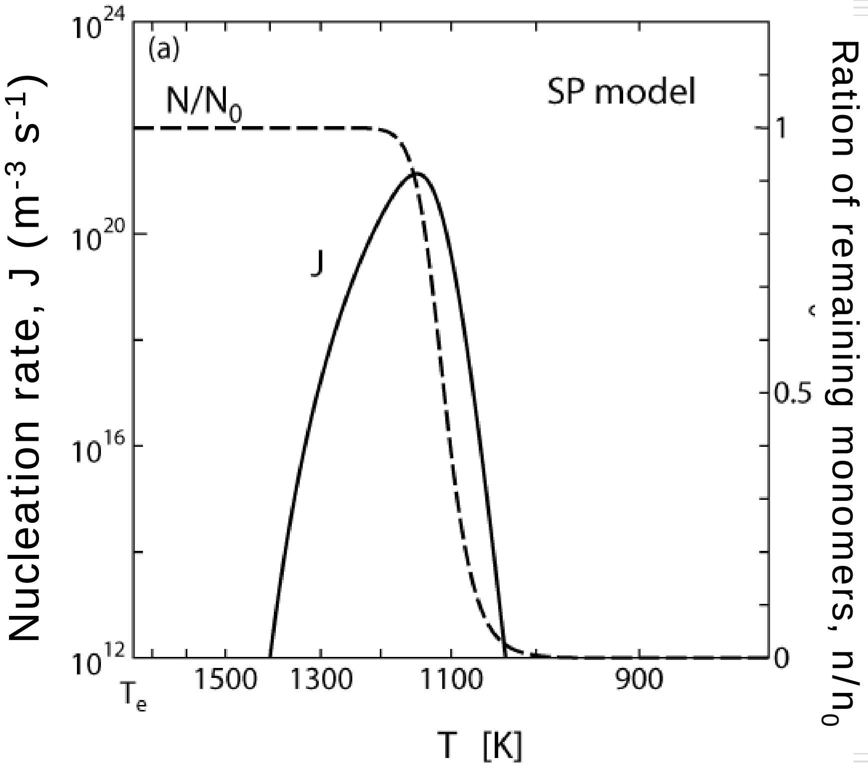
- Dissociation energy of dimer: 2700 K

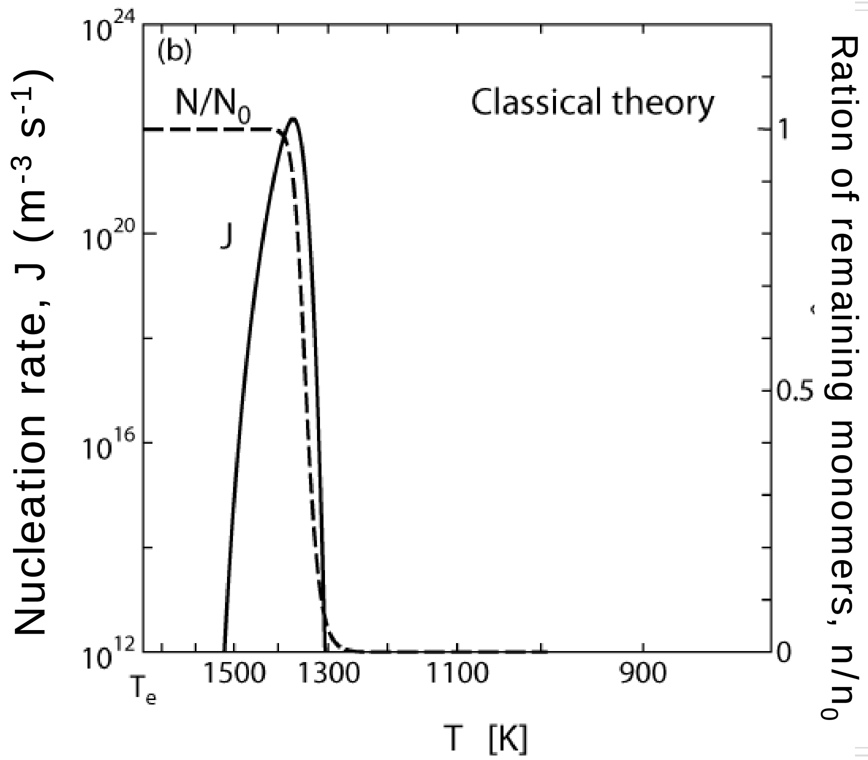
A. Kant, S.-S. Lin, and B. Strauss Dissociation energy of Mn2 J. Chem. Phys. vol.49, p1983-1985, 1968

- Equilibrium distance between nuclei: $Re = 2.34 \times 10^{-8}$ cm
- Vibrational frequency: 1×10^{13} s^{-1}

Dissociation energies of diatomic molecules of the transition elements. II Titanium, Chromium, Manganese, and Cobalt J. Chem. Phys. vol.41, p.3806-3808, 1964

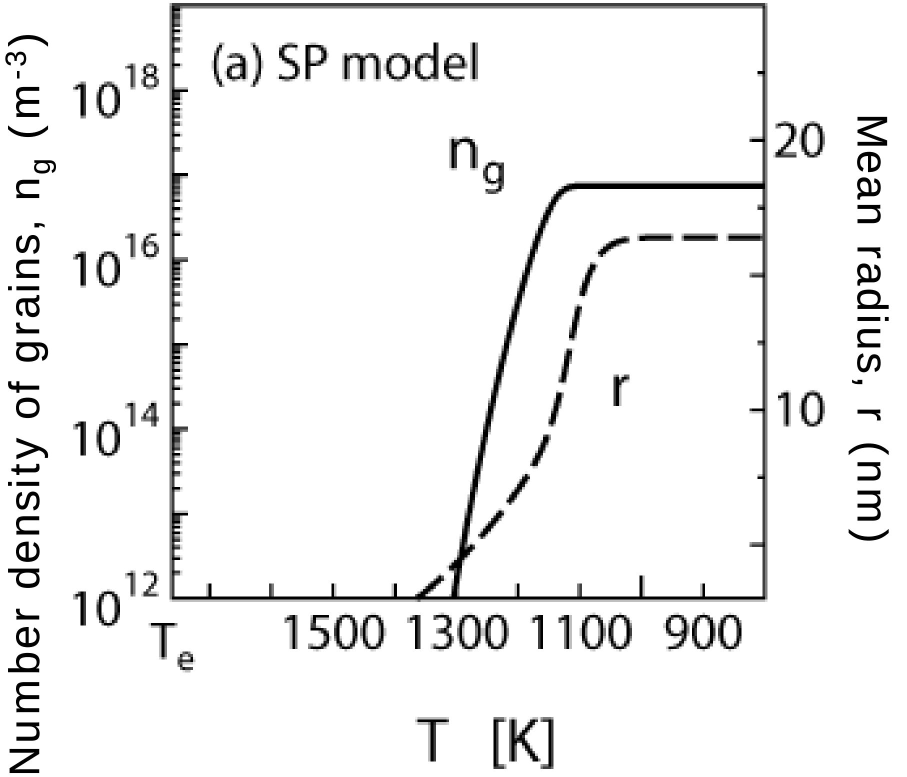
Condensation Temperature

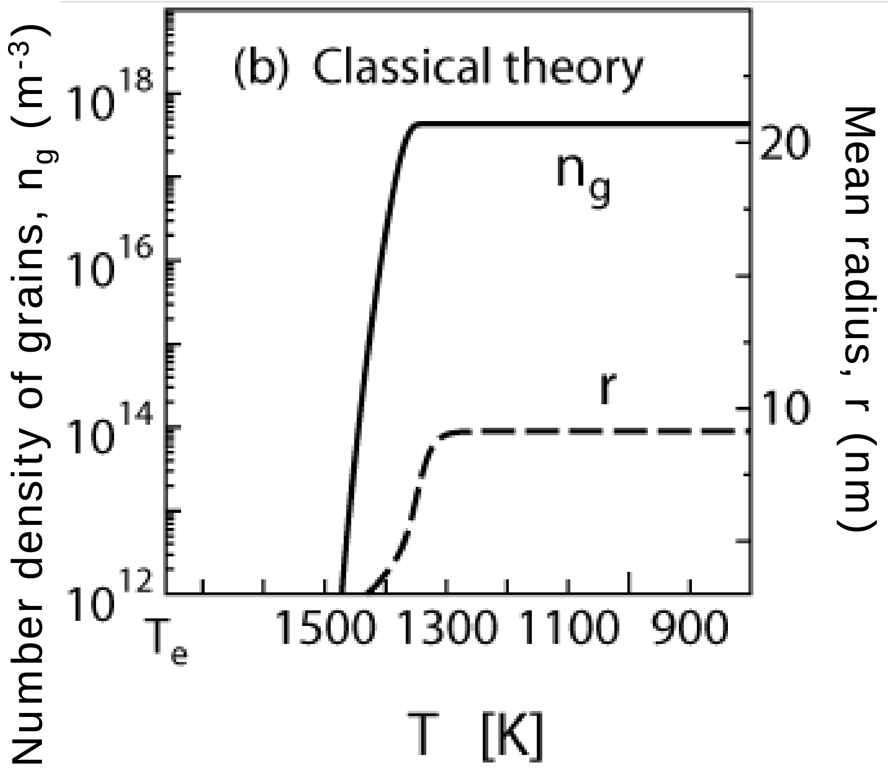




	Experiment	SP Model	CNT
Condensation *T* :	1100 K	**1110 K**	1340 K
Number density:	6×10^{15} m^{-3}	**7.5×10^{16}** m^{-3}	4.3×10^{17} m^{-3}
Mean radius :	13.7 nm	**16 nm**	9.1 nm

Number density & Size





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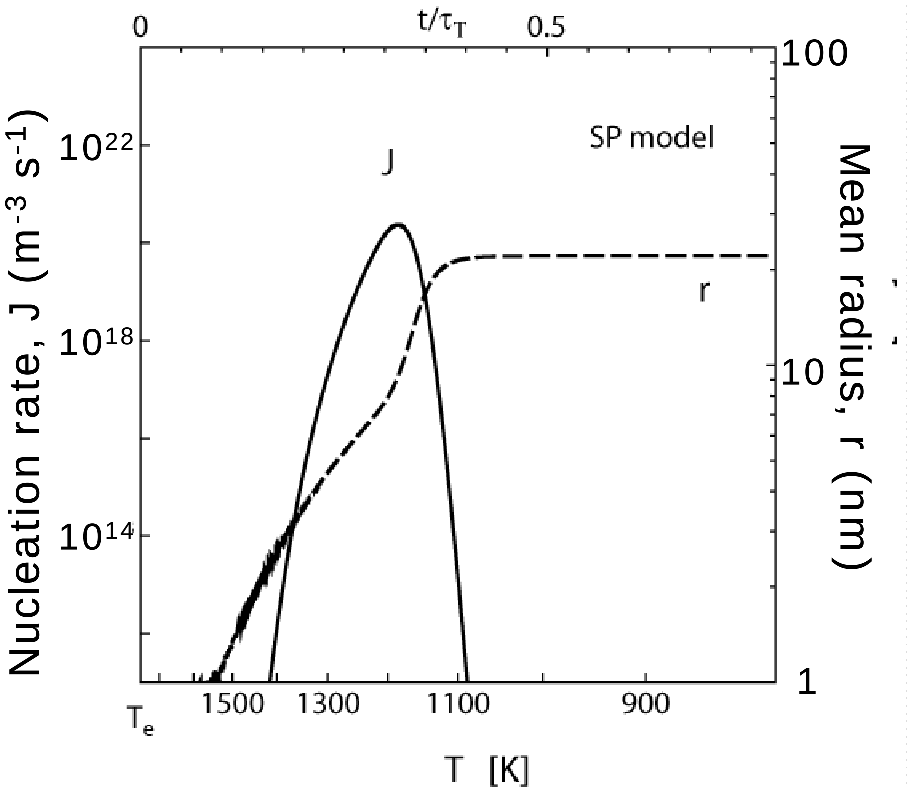
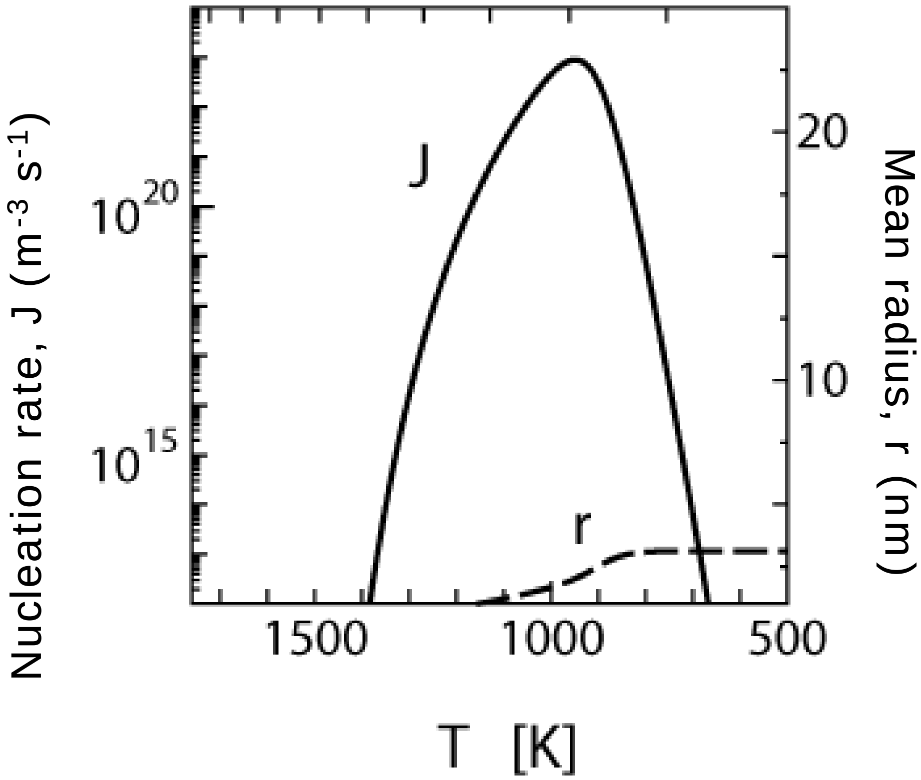
Mean radius :	13.7 nm	**16 nm**	9.1 nm

Surface free *E* can be determined using condensation *T*.

Validity of a Sticking coefficient





	Experiment	SP Model	SP Model
Sticking provability:		1.0	0.1
Condensation *T* :	1100 K	1110 K	898 K
Mean radius :	13.7 nm	16 nm	3.1 nm

Validity of a Sticking coefficient

We assumed the sticking coefficient is unity, which will be confirmed from growth rate and timescale for growth.

- Growth velocity: $R = \dfrac{\alpha\Omega (P - P_e)}{(2\pi m k T)^{1/2}}$, Hertz-Knudsen's equation.

$\Omega_{\text{(volume of molecule)}}$: 1.22×10^{-23} cm^{-3}
$P_{\text{(vapor pressure)}}$: 2.7×10^{4} dyne cm^{-2}
$P_{e\text{(equilibrium vapor pressure)}}$: 4.4×10^{-1} dyne cm^{-2}
$m_{\text{(molecular weight)}}$: 9.11×10^{-23} g
$K_{\text{(Boltzman constant)}}$: 1.38×10^{-16} erg K^{-1}
$T_{\text{(absorute temperature)}}$: 1100 K

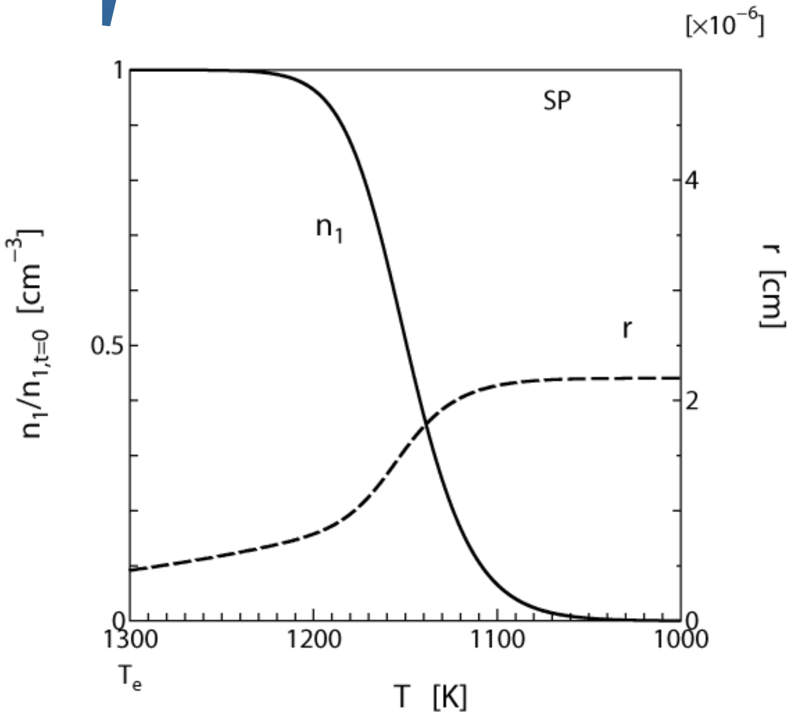
When α is unity,

$R = 3.5\times10^{5}$ nm s^{-1}

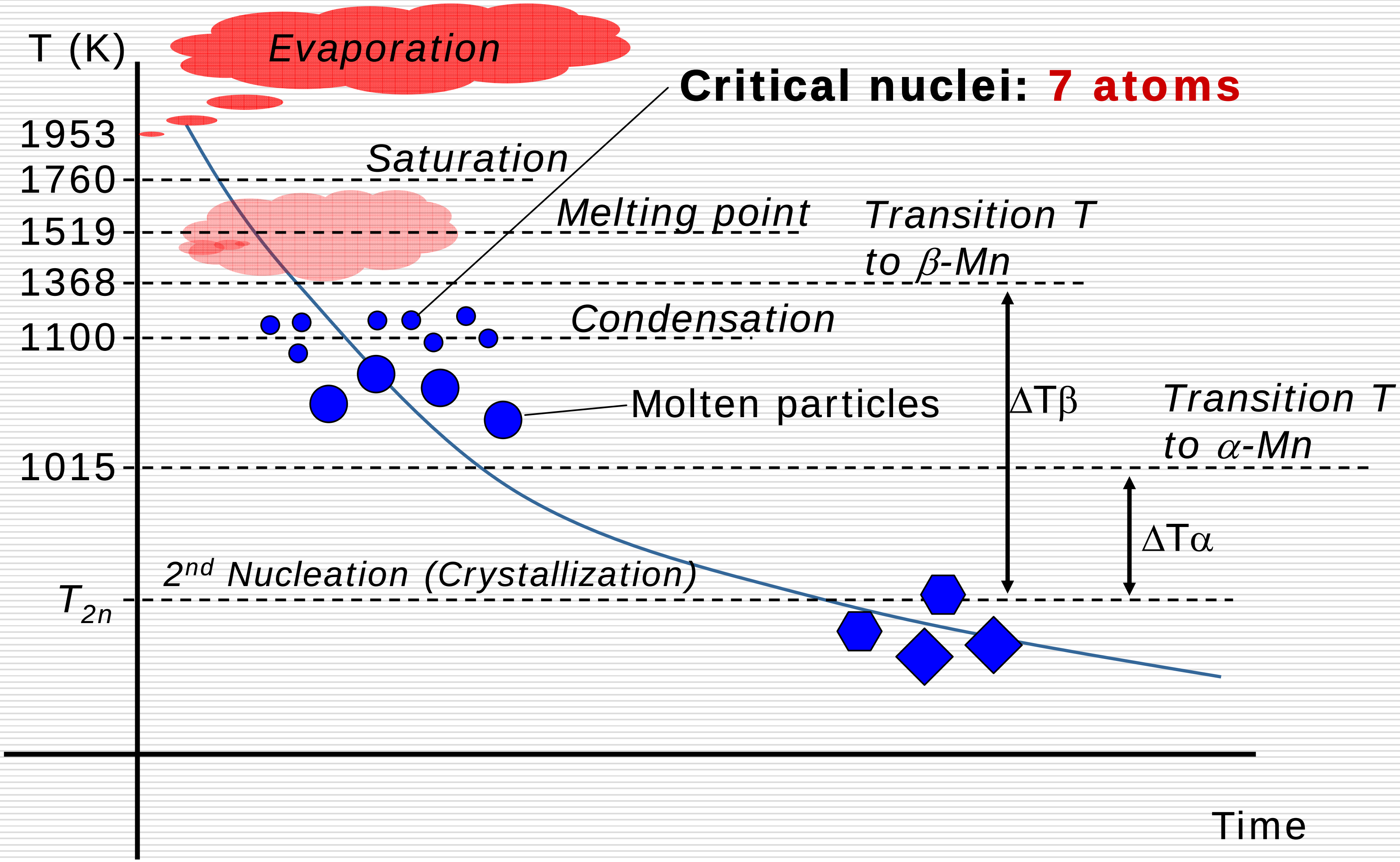
Time scale for grains growth corresponds to timescale for gas cooling for 100 K, 1×10^{-4} s.

Mn particles can be grown to 35 nm.

α will be 14 / 35 = 0.4.



Formation process of Mn nanoparticles



Conclusion

- Condensation occurs under very high supercooling (ΔT=660K).
- Supersaturation is as high as 10^4-10^5.
- SP model works well.
- Sticking probability can be determined.

In Dec., 2011

Dec., 2012