The effect of thermal non-equilibrium on kinetic nucleation

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KU LEUVEN ÖAW ÖSTERREICHISCHE AKADEMIE DER WISSENSCHAFTEN IWF INSTITUT FÜR WELTRAUMFORSCHUNG TU Graz MARIE CURIE ACTIONS

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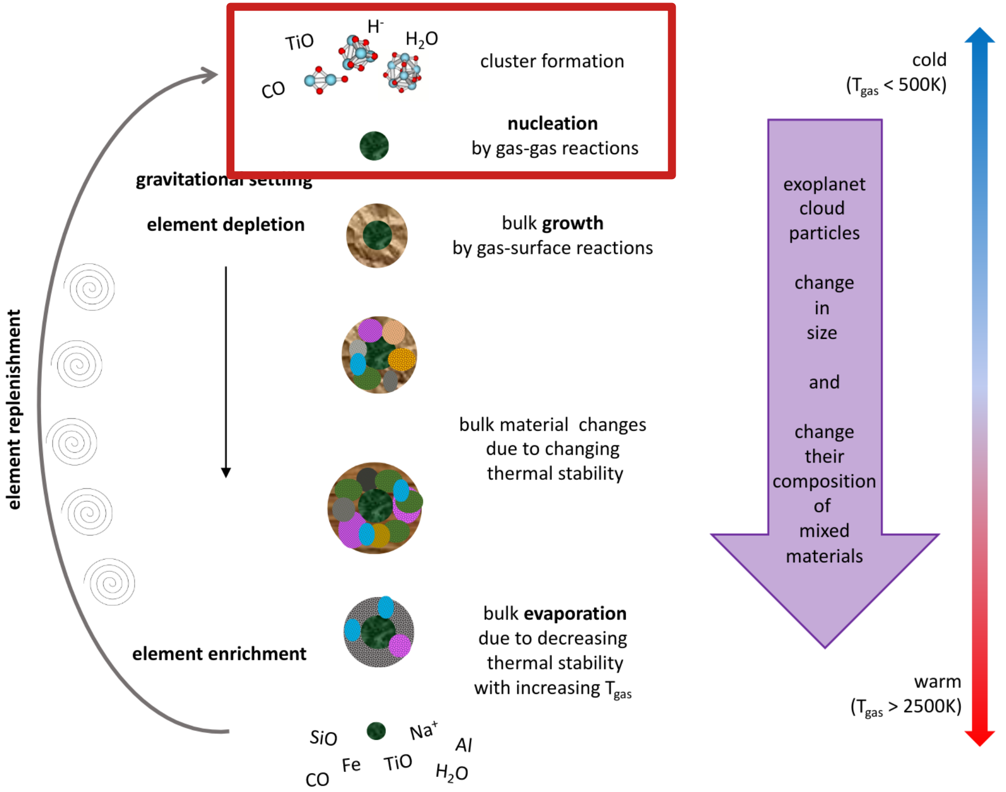
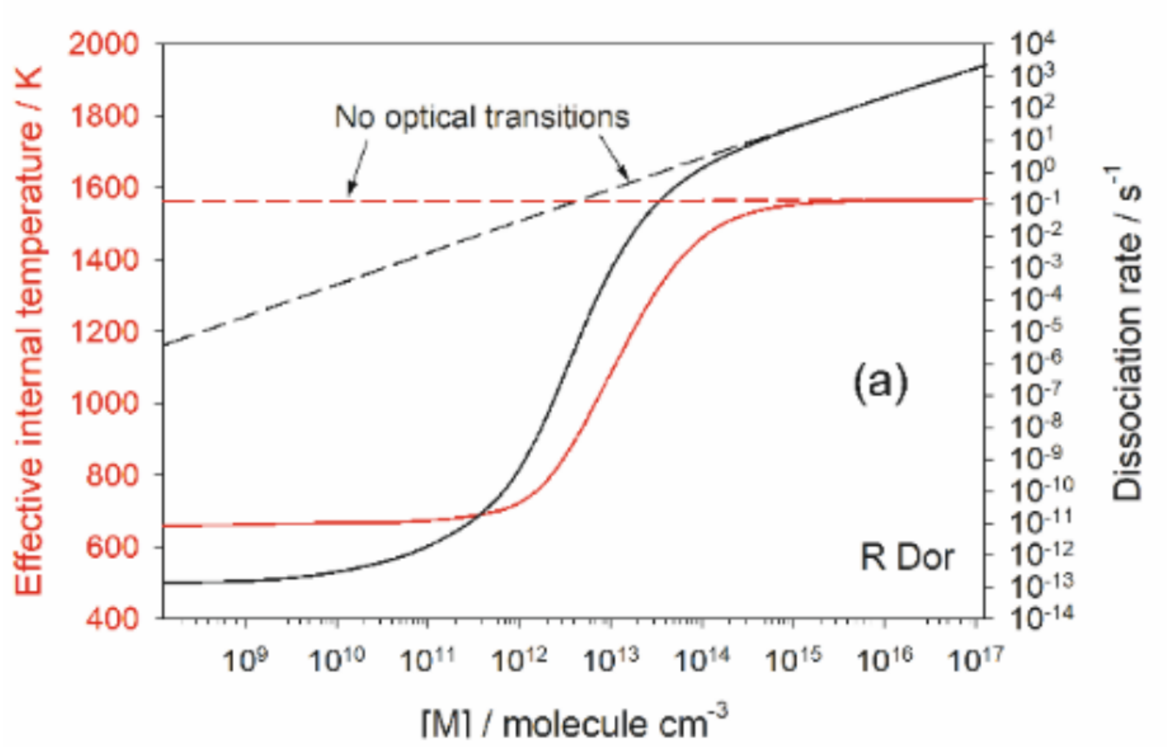
Overview

- Where to find thermal non-equilibrium
- How to nucleate
- Thermal non-equilibrium
- The effect of thermal non-equilibrium



Helling (2019)

Where to find thermal non-equilibrium



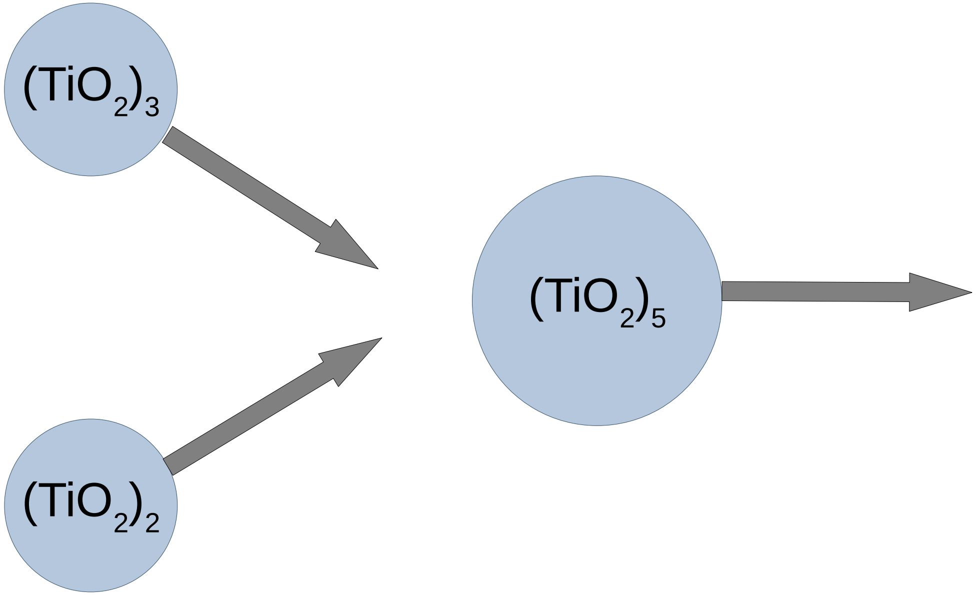
Plane and Robertson 2022:

- Outflows of AGB stars
- Dissociation of $OSi(OH)_2$
- Internal cooling via optical lines

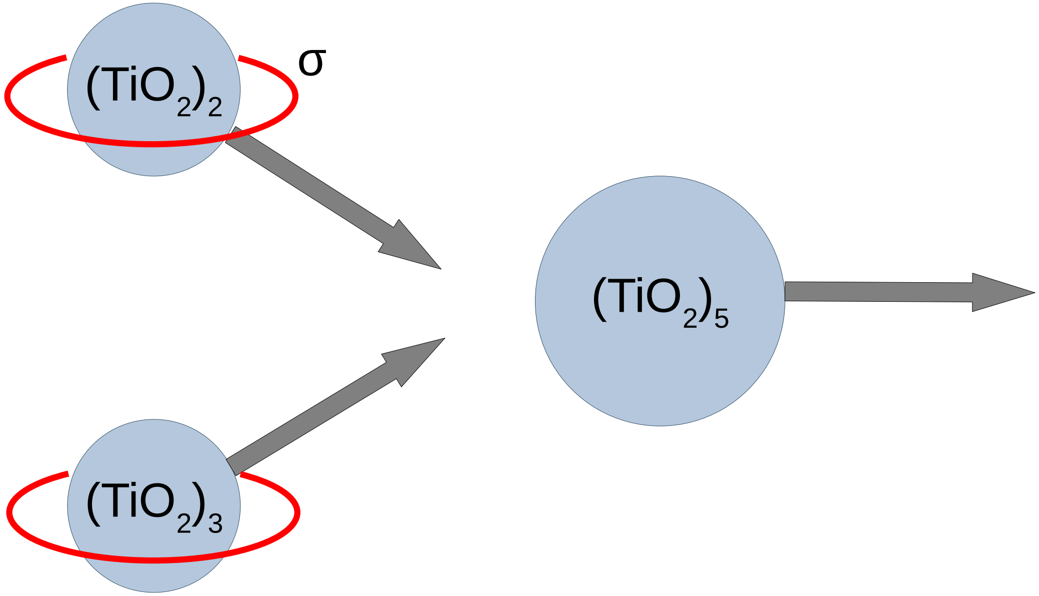
Observational evidence:

- Fonfria et al. 2008, 2017, 2021

How to nucleate



How to nucleate



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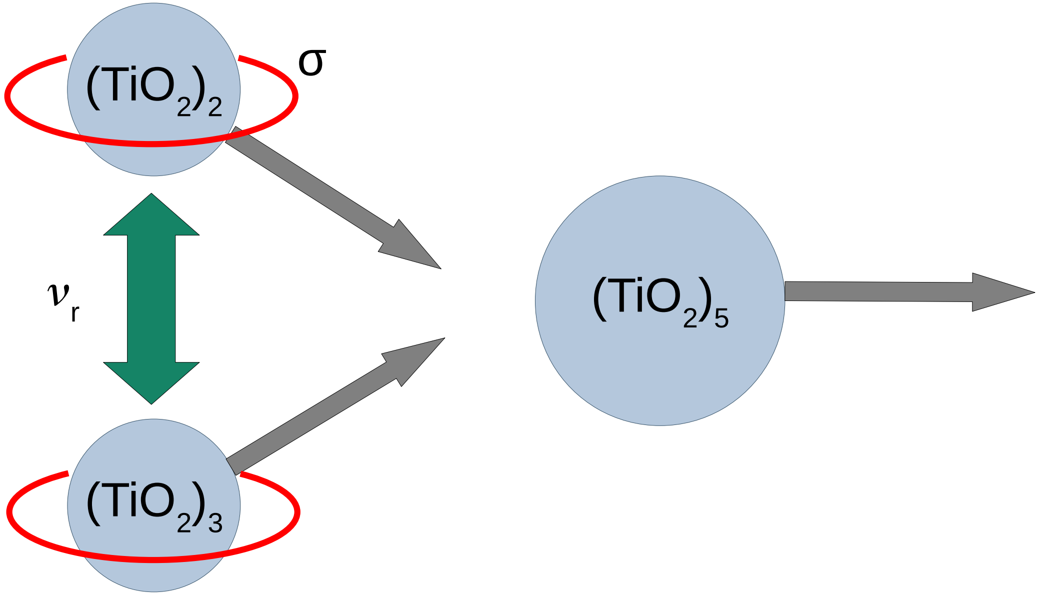

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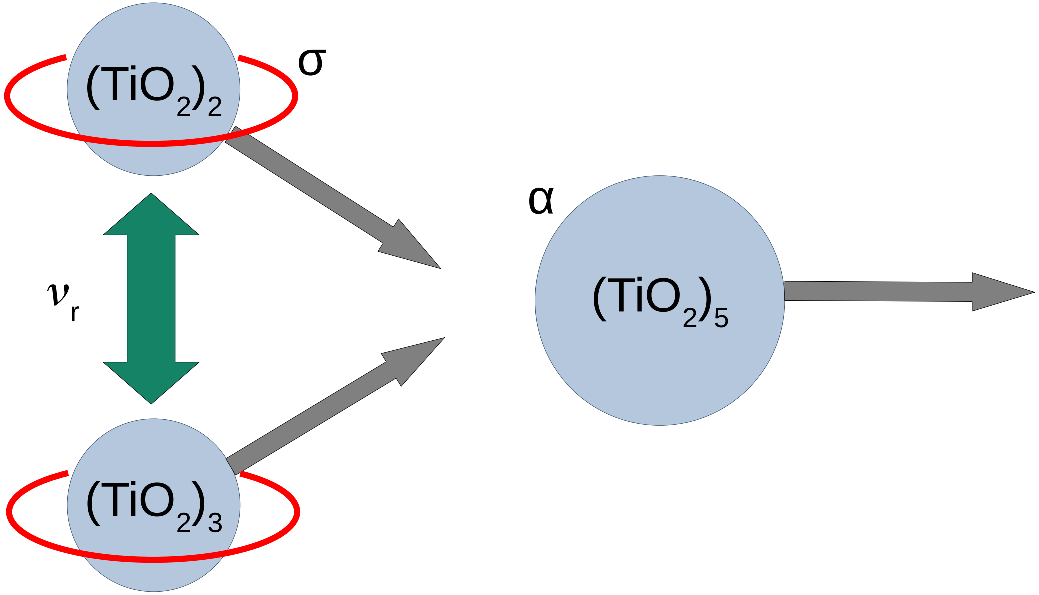
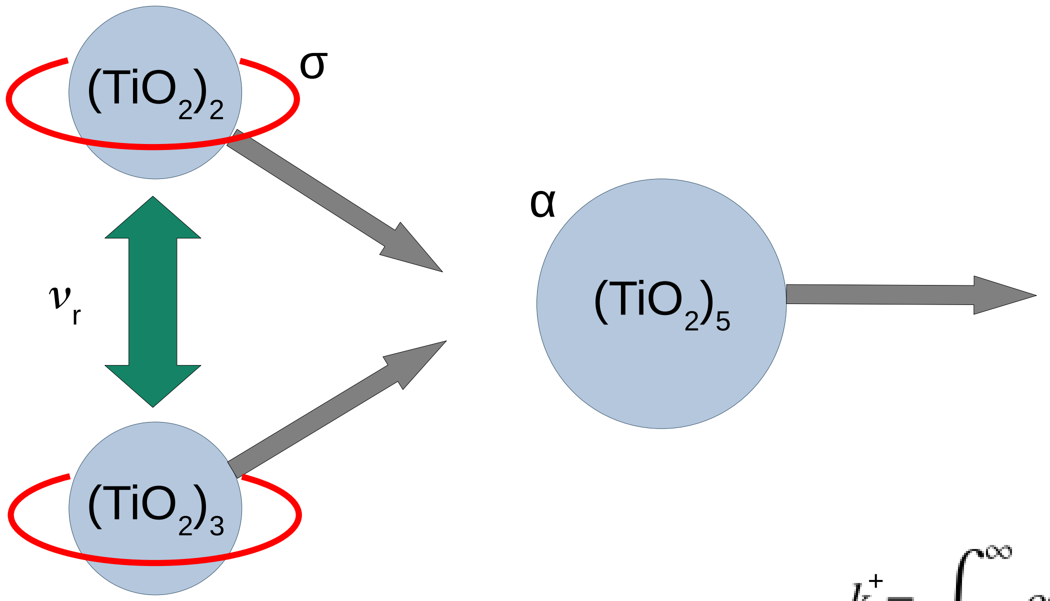
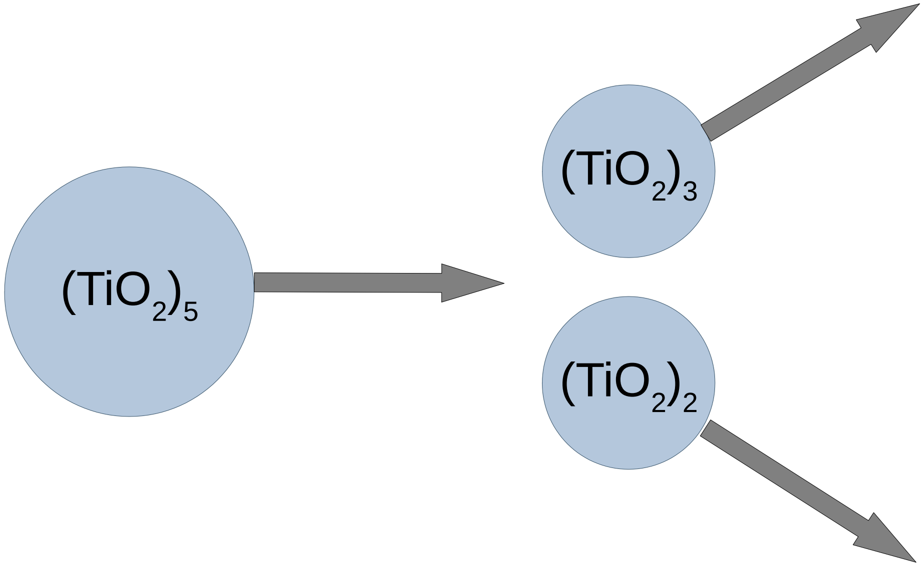


How to nucleate

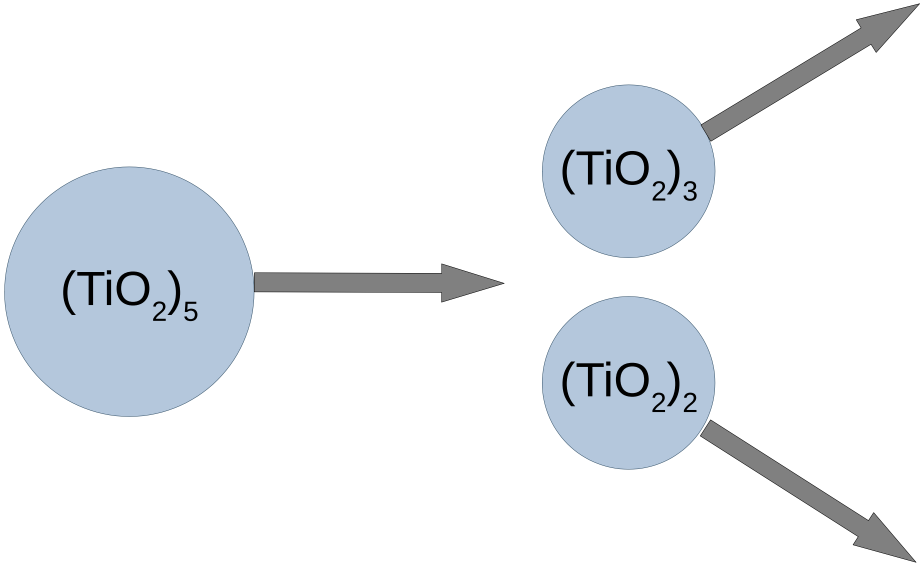


$$k^{+} = \int_0^{\infty} \alpha(\nu_r)\, \sigma(\nu_r)\, \nu_r\, f(\nu_r)\, d\nu_r$$

How to nucleate



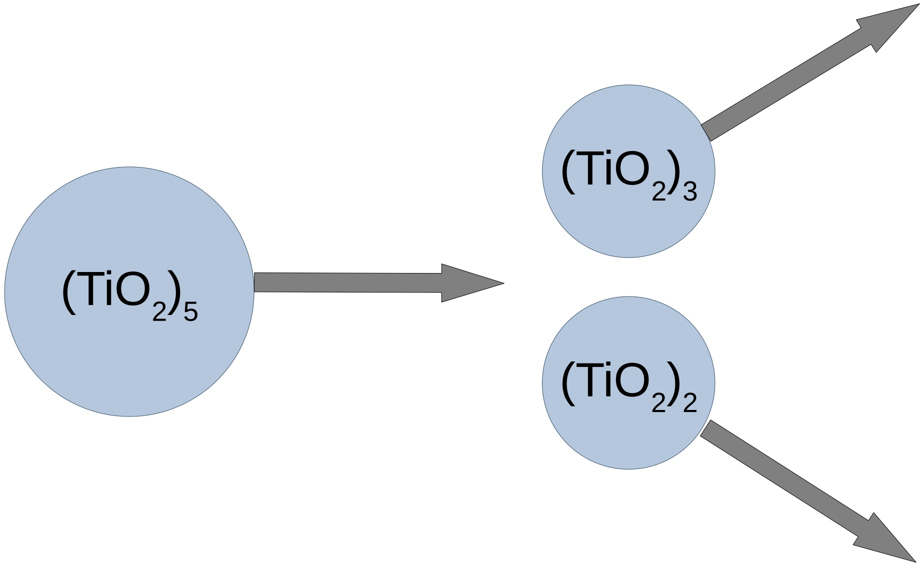
How to nucleate



Detailed balance in chemical equilibrium:

$$\frac{k^{-}_{N,M}}{k^{+}_{N,M}} = \frac{n^{\mathrm{eq}}_{N} n^{\mathrm{eq}}_{M}}{n^{\mathrm{eq}}_{N+M}}$$

How to nucleate



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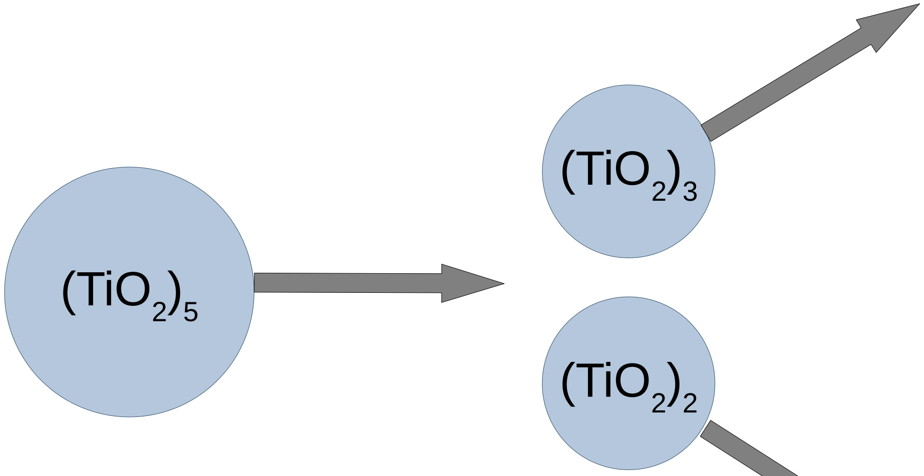
Law of mass action in thermal equilibrium:

$$\frac{n^{\mathrm{eq}}_N\, n^{\mathrm{eq}}_M}{n^{\mathrm{eq}}_{N+M}} = \frac{P^\circ}{k_{\mathrm{B}}T} \exp\left(\frac{G^\circ_{N+M} - G^\circ_M - G^\circ_N}{k_{\mathrm{B}}T}\right)$$

How to nucleate



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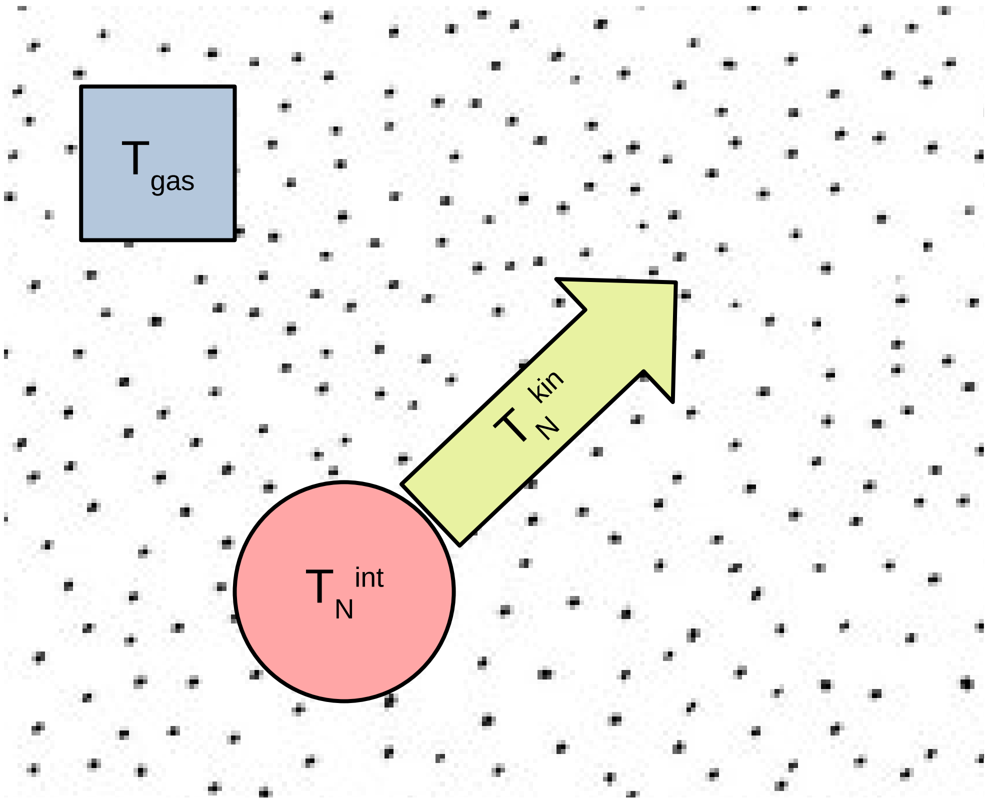
Backward rate:

$$k^-_{N,M} = k^+_{N,M} \frac{P^\circ}{k_\mathrm{B}T} \exp\left(\frac{G^\circ_{N+M} - G^\circ_M - G^\circ_N}{k_\mathrm{B}T}\right)$$

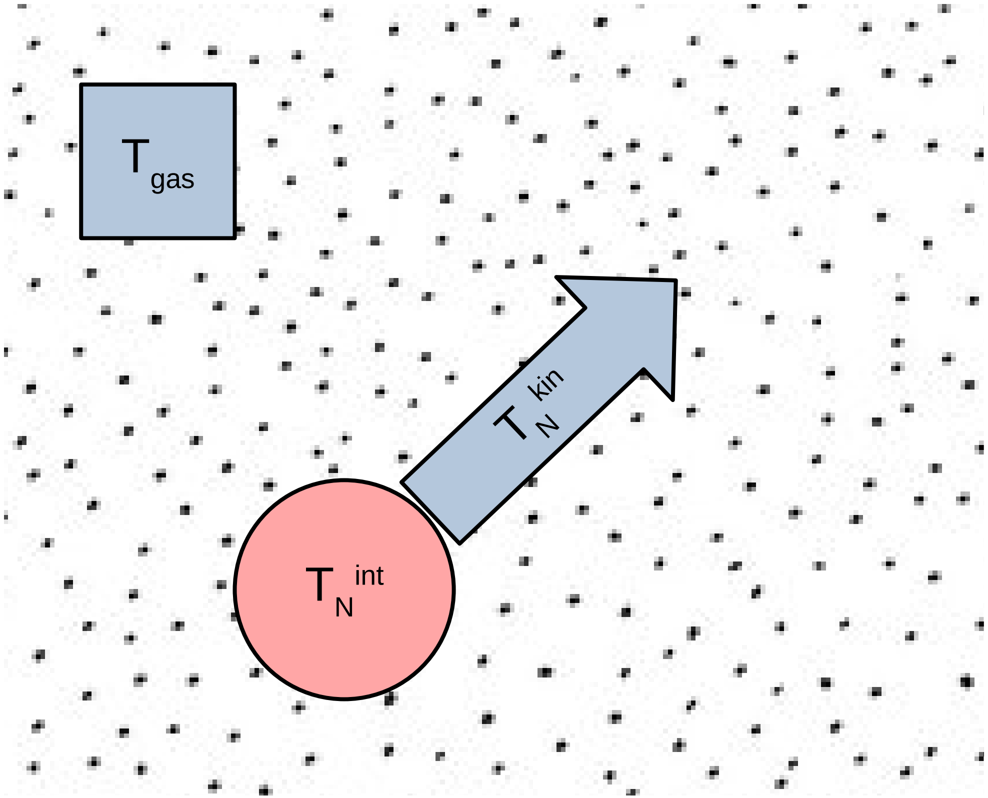
Thermal non-equilibrium



Types of thermal non-equilibrium:

- $T_{gas} \neq T_N^{kin} \neq T_N^{int}$
  → Kiefer et al. 2023

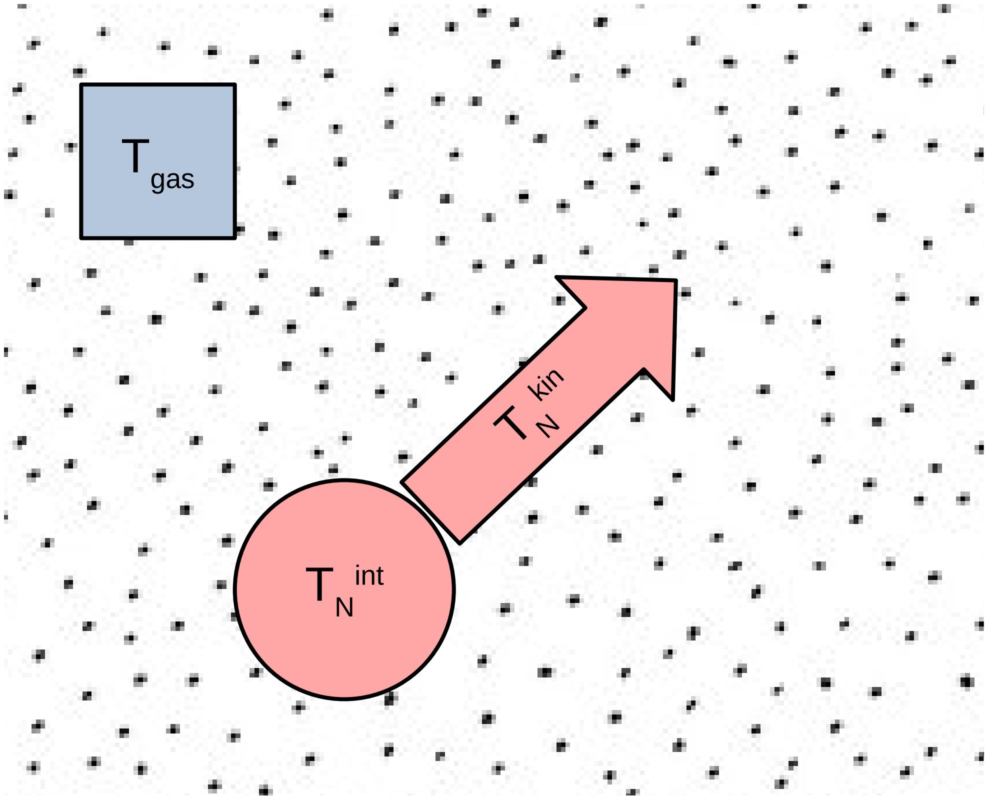
Thermal non-equilibrium



Types of thermal non-equilibrium:

- $T_{gas} \neq T_N^{kin} \neq T_N^{int}$
  → Kiefer et al. 2023
- $T_{gas} = T_N^{kin} \neq T_N^{int}$
  → Plane et al. 2022

Thermal non-equilibrium



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  → Kiefer et al. 2023
- $T_{gas} = T_N^{kin} \neq T_N^{int}$
  → Plane et al. 2022
- $T_{gas} \neq T_N^{kin} = T_N^{int}$
  → Patzer et al. 1998
  → Köhn et al. 2021

Thermal non-equilibrium

Thermal equilibrium

$$k^{+} = \int_0^\infty \alpha(\nu_r)\, \sigma(\nu_r)\, \nu_r\, f(\nu_r)\, d\nu_r$$

$$k^{-}_{N,M} = k^{+}_{N,M} \frac{P^\circ}{k_\mathrm{B} T} \exp\left(\frac{G^\circ_{N+M} - G^\circ_M - G^\circ_N}{k_\mathrm{B} T} \right)$$

Full derivation can be found in:
"The effect of thermal non-equilibrium on kinetic nucleation" - Kiefer et al. 2023

Thermal non-equilibrium

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Thermal non-equilibrium

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$$k^{-} = k^{+} \frac{p^\circ}{k T_\mathrm{gas}} A\ B\ C$$

$$A = \exp\left(\sum_{i \in \zeta} \frac{\delta(i)}{k T_i^\mathrm{kin}} \left[G_i^\circ(T_\mathrm{gas}) - i G_1^\circ(T_i^\mathrm{kin}) + k(T_i^\mathrm{kin} - T_\mathrm{gas}) \right] \right)$$

$$B = \exp\left(\sum_{i \in \zeta} \frac{\delta(i)}{k T_i^\mathrm{kin}} \omega_i(T_i^\mathrm{kin}, T_i^\mathrm{int}) \right)$$

$$C = \left(\frac{k T_\mathrm{gas} n_1^\mathrm{eq}}{p^\circ} \right)^{- \sum_{i \in \zeta} \delta(i) i \frac{T_\mathrm{gas}}{T_i^\mathrm{kin}}}$$

$T^{\mathrm{gas}} = T^{\mathrm{kin}} = T^{\mathrm{kin}}$

Thermal non-equilibrium

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$T^{gas} = T^{kin} = T^{kin}$

$T^{gas} \neq T^{kin}$

Thermal non-equilibrium

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Thermal non-equilibrium

$T^{gas} = T^{kin} = T^{kin}$

$T^{gas} \neq T^{kin}$

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Thermal equilibrium

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Thermal non-equilibrium

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Gauge

Thermal equilibrium

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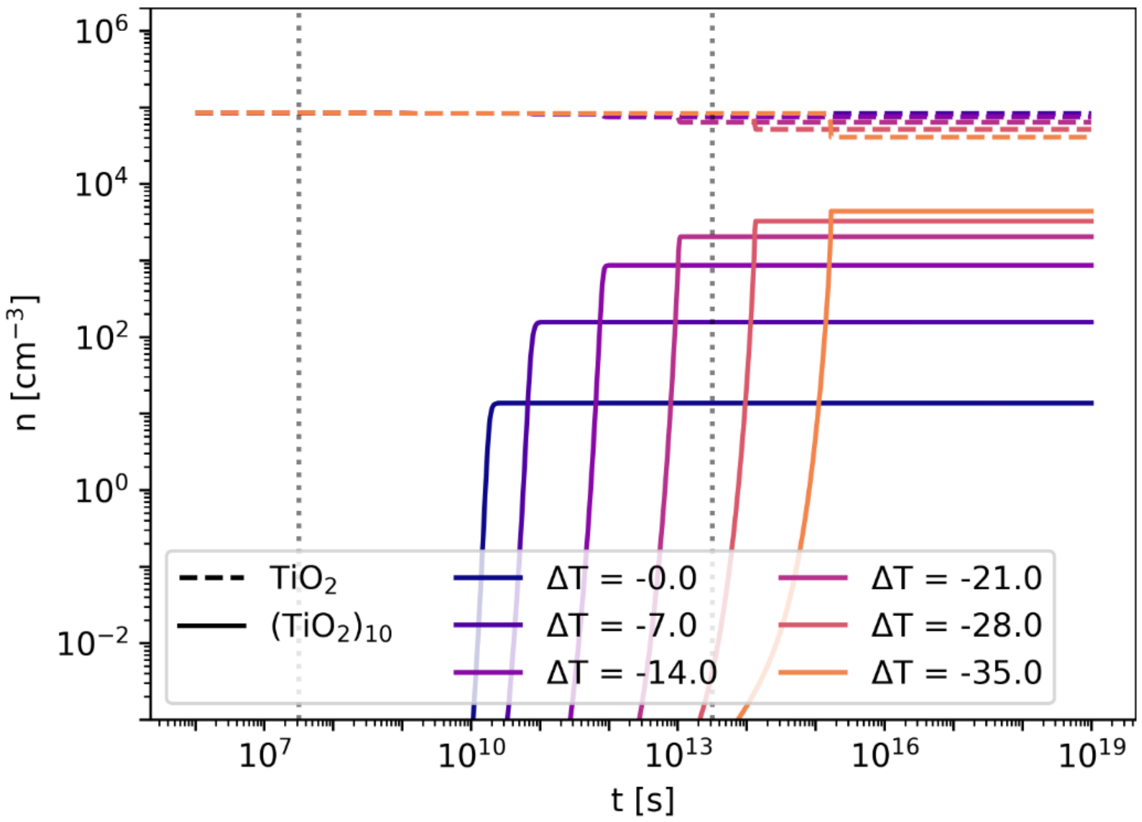
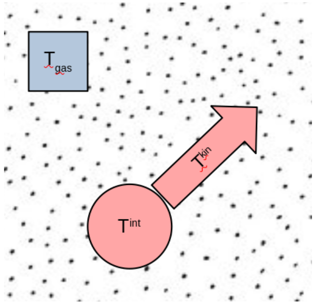
The effect of thermal non-equilibrium





$$T_{\text{gas}} = 1250\ \text{K}$$

$$\Delta T = T^{\text{kin}}_{(\text{TiO}_2)_{10}} - T^{\text{kin}}_{\text{TiO}_2}$$

$$T^{\text{kin}}_N = T_{\text{gas}} + \frac{e^{N-1} - 1}{e^9 - 1} \Delta T$$

- Small temperature offsets can cause significant change in the number density of larger clusters.
- The change in number density depends on the thermal non-equilibrium present.
- Thermal non-equilibrium can both increase (ΔT<0) or decrease (ΔT>0) the formation of larger clusters.

Summary

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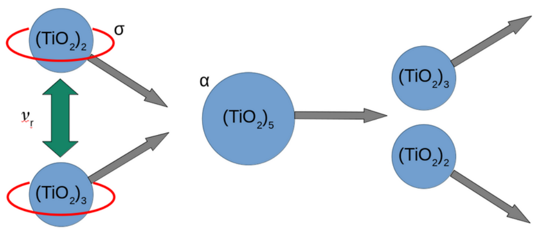
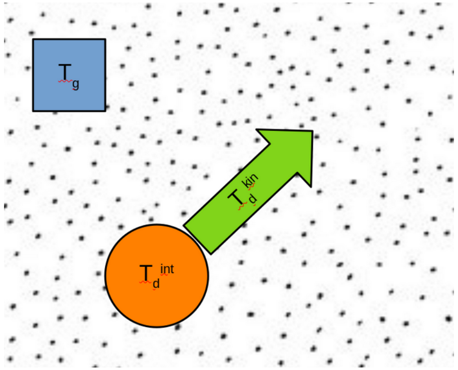
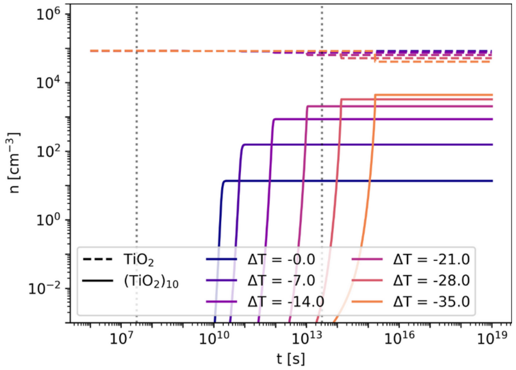
Kinetic nucleation can describe the formation of clusters under non-equilibrium conditions



Multiple types of thermal non-equilibrium are studied



Small temperature offsets can change the number density of clusters significantly



Check out the paper:
"The effect of thermal non-equilibrium on kinetic nucleation" - Kiefer et al. 2023

Additional Slides

How to nucleate

$n_{(TiO2)5}$

↑

$$\frac{dn_s}{dt} = \sum_{j \in \mathcal{F}_s} \left(k_j \prod_{r \in \mathcal{R}_j} n_r \right) - \sum_{j \in \mathcal{D}_s} \left(k_j \prod_{r \in \mathcal{R}_j} n_r \right)$$

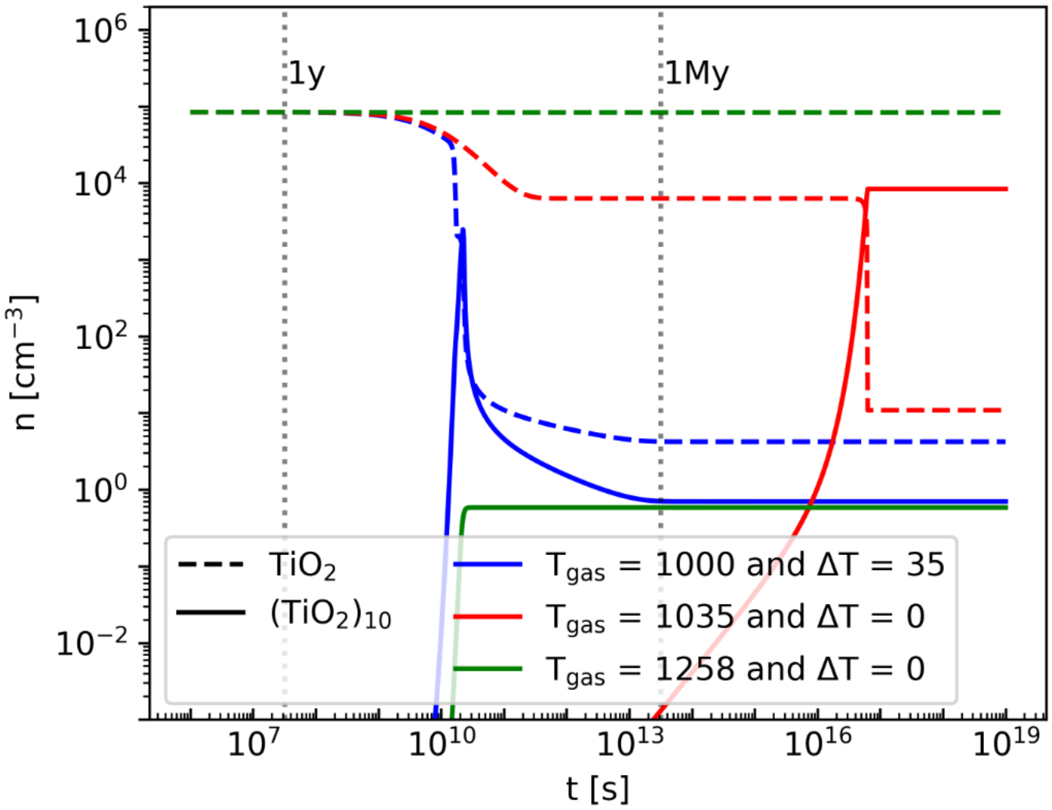
↓ ↓

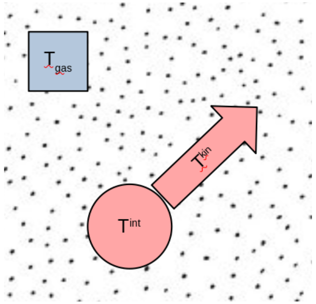
$k^{+}_{(2,3)}\, n_{(TiO2)2}\, n_{(TiO2)3}$ $k^{-}_{(2,3)}\, n_{(TiO2)5}$

Nucleation network:

- Set of reactions that includes a formation path for larger cluster
- For reactions only involving clusters of size smaller than 4, we consider termolecular associations (3-Body reactions)
- For larger clusters, we consider bimolecular radiative associations (2-Body reactions)
- Backward rates are derived using detailed balance and the law of mass action

The effect of thermal non-equilibrium





How to nucleate

$n_{(TiO2)5}$

$$\frac{dn_s}{dt} = \sum_{j\in\mathcal{F}_s}\left(k_j \prod_{r\in\mathcal{R}_j} n_r\right) - \sum_{j\in\mathcal{D}_s}\left(k_j \prod_{r\in\mathcal{R}_j} n_r\right)$$

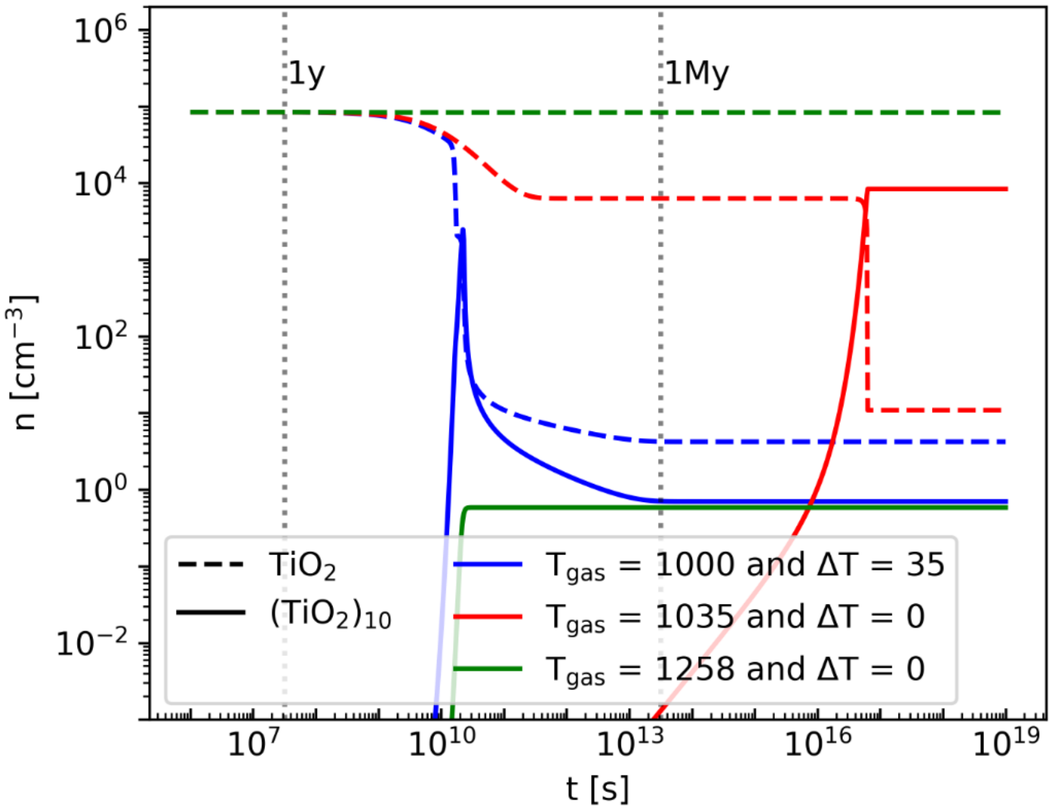
$k^+_{(2,3)}\ n_{(TiO2)2}\ n_{(TiO2)3}$

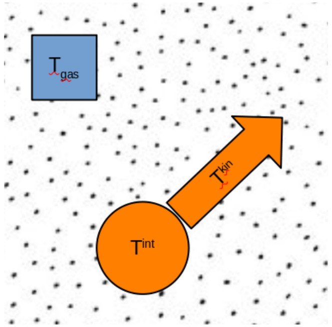
$k^-_{(5,2)}\ n_{(TiO2)7}$

$k^-_{(2,3)}\ n_{(TiO2)5}$

$k^+_{(5,2)}\ n_{(TiO2)5}\ n_{(TiO2)2}$

The effect of thermal non-equilibrium

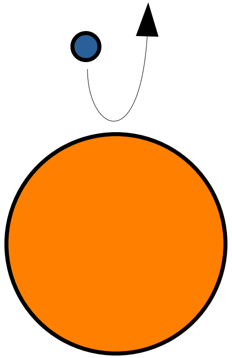




Thermal adjustments

- Kinetic – Collisonal

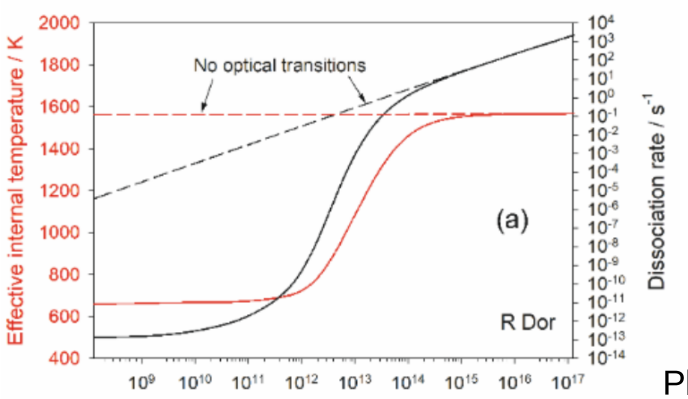
$$(\tau_{\rm gc}^{\rm int})^{-1} \approx \frac{2\bar{\alpha}_T}{D_f} n_{\rm gas} r_{\rm N}^2 \sqrt{\frac{8\pi k T_{\rm gas}}{m_{\rm gas}}}$$

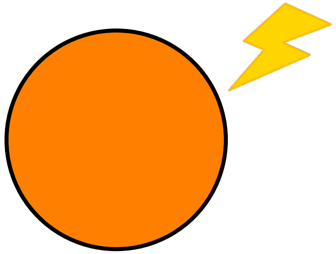


- Internal – Collisonal

$$(\tau_{\rm gc}^{\rm kin})^{-1} \approx \frac{8 m_{\rm gas}}{3 m_N} n_{\rm gas} \pi r_N^2 \sqrt{\frac{8 k T_{\rm gas}}{\pi m_{\rm gas}}}$$

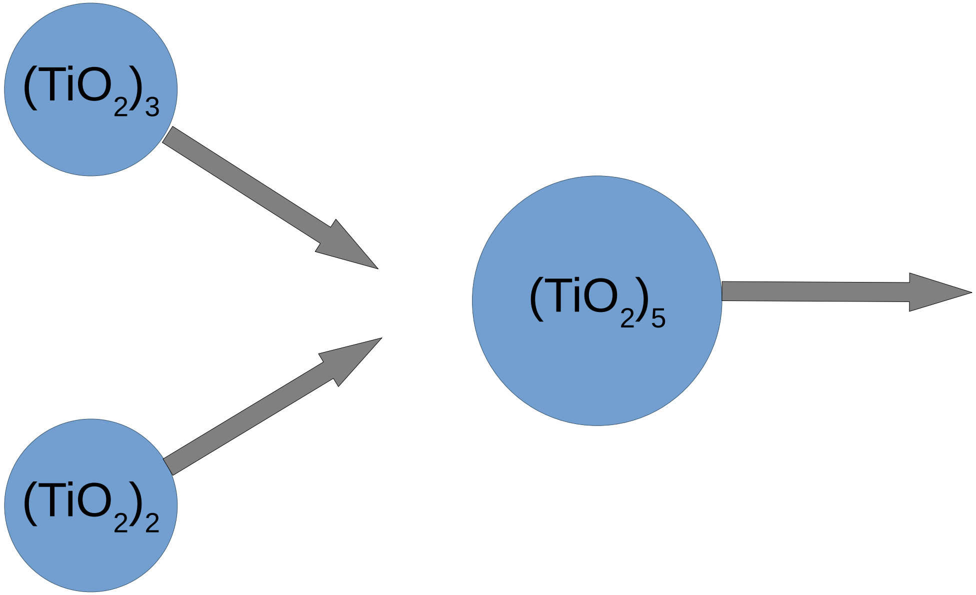
- Internal – Radiative





Plane et al. 2022

Inelastic collisions

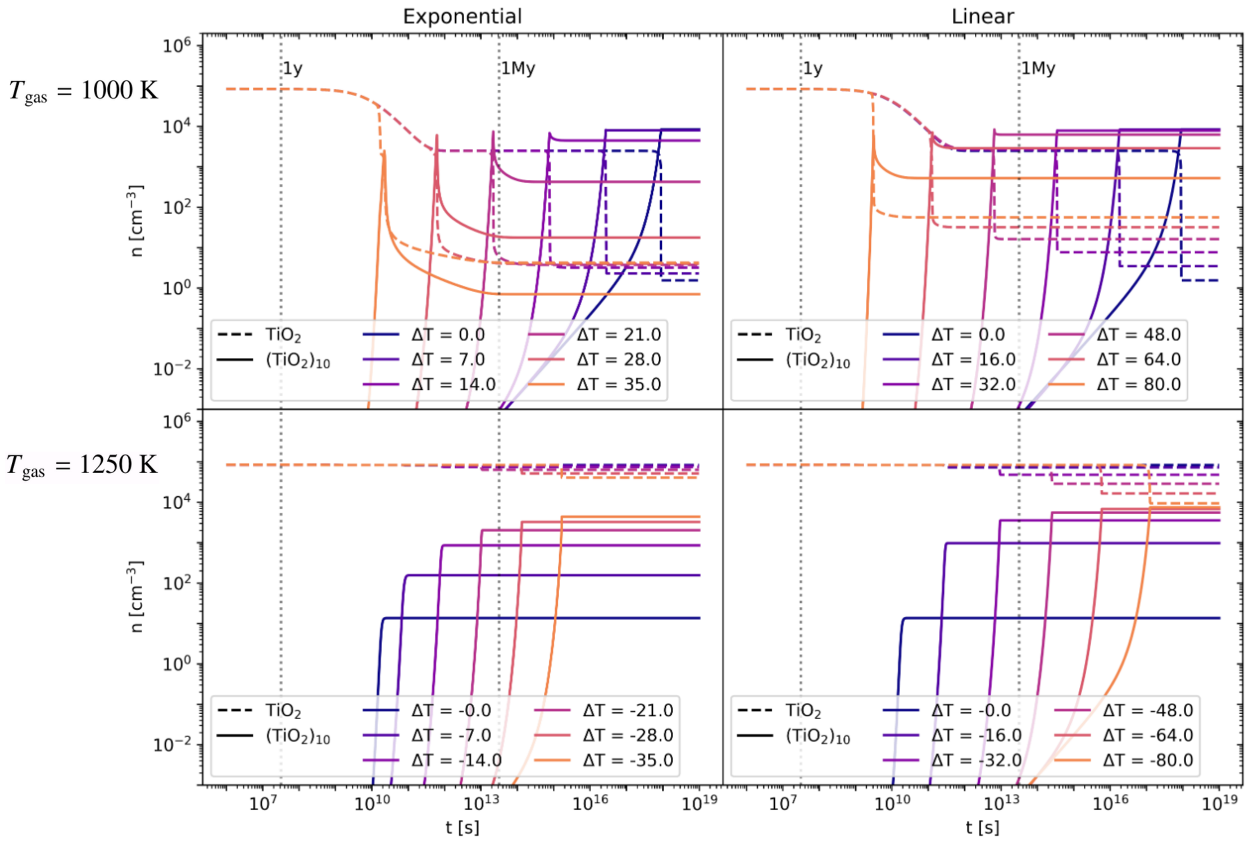


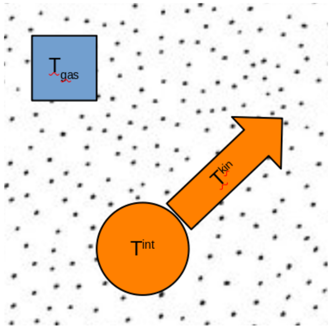
$$T^{\mathrm{kin}} = \frac{(m_1 + m_2)}{\tilde{\mu}} = \frac{m_1 T_1^{\mathrm{kin}} + m_2 T_2^{\mathrm{kin}}}{(m_1 + m_2)} = T_1^{\mathrm{kin}} + T_2^{\mathrm{kin}} - \frac{\mu}{\mu_T}$$

$$\Delta E^{\mathrm{kin}} = \frac{3k}{2}(T_N^{\mathrm{kin}} + T_M^{\mathrm{kin}} - T_{M+N}^{\mathrm{kin}}) = \frac{3k}{2}\frac{\mu}{\mu_T}$$

$$\Delta T_{\mathrm{inel}}^{\mathrm{int}} = \frac{2}{D_f k}\left(\Delta E_{\mathrm{inel}}^{\mathrm{kin}} + \Delta E_{\mathrm{frebind}}\right) = \frac{2}{D_f k}\left(\frac{3k\mu}{2\mu_T} + \Delta E_{\mathrm{bind}}\right)$$

The effect of thermal non-equilibrium





$$\Delta T = T^{\text{kin}}_{(\text{TiO}_2)_{10}} - T^{\text{kin}}_{\text{TiO}_2}$$

$$T^{\text{kin}}_N = T_{\text{gas}} + \frac{e^{N-1} - 1}{e^9 - 1}\Delta T$$

$$T^{\text{kin}}_N = T_{\text{gas}} + \frac{(N-1)}{9}\Delta T$$

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Derivation of the Backward rate

$$G^{non-eq}(T_0^{\mathrm{int}},\ldots,T_r^{\mathrm{int}},T_0^{\mathrm{kin}},\ldots,T_r^{\mathrm{kin}},p_0,\ldots,p_r,N_0,\ldots,N_r) = \sum_{i=0}^{r} G_i^{non-eq}(T_i^{\mathrm{int}},T_i^{\mathrm{kin}},p_i,N_i) = \sum_{i=0}^{r} G_i(T_i^{\mathrm{kin}},p_i,N_i) + N_i\,\omega_i(T_i^{\mathrm{kin}},T_i^{\mathrm{int}}),$$

$$C = \sum_{i=1}^{r} i\,N_i$$

$$G = N\mu$$

$$\mathcal{L} = N_{\mathrm{gas}}\mu_{\mathrm{gas}}(T_{\mathrm{gas}},p) + N_{\mathrm{gas}}kT_{\mathrm{gas}}\ln\left(\frac{N_{\mathrm{gas}}}{N}\right) - \lambda C + \sum_{i=1}^{r} N_i\mu_i(T_i^{\mathrm{kin}},p) + N_ikT_i^{\mathrm{kin}}\ln\left(\frac{N_i}{N}\right) + N_i\,\omega_i(T_i^{\mathrm{kin}},T_i^{\mathrm{int}}) + \lambda i N_i.$$

$$N_{\mathrm{gas}} \gg \sum_{i=1}^{r} N_i$$

$$N_{\mathrm{gas}}T_{\mathrm{gas}} \gg \sum_{i=1}^{r} N_iT_i^{\mathrm{kin}}$$

$$\frac{\partial\mathcal{L}}{\partial N_j} = \mu_j(T_j^{\mathrm{kin}},p) + kT_j^{\mathrm{kin}}\ln\left(\frac{N_j}{N}\right) + \omega_j(T_j^{\mathrm{kin}},T_j^{\mathrm{int}}) + \lambda j x_1 + kT_j^{\mathrm{kin}}\frac{N-N_j}{N} - \sum_{\substack{i=0\\ i\neq j}}^{r}\frac{N_ikT_i^{\mathrm{kin}}}{N},$$

$$\approx \mu_j(T_j^{\mathrm{kin}},p) + kT_j^{\mathrm{kin}}\ln\left(\frac{N_j}{N}\right) + \omega_j(T_j^{\mathrm{kin}},T_j^{\mathrm{int}}) + \lambda j + k(T_j^{\mathrm{kin}} - T_{\mathrm{gas}}),$$

$$\lambda = -\mu_1(T_{\mathrm{gas}},p) - kT_{\mathrm{gas}}\ln\left(\frac{N_1}{N}\right)$$

$$\frac{\mathring{N}_j}{\mathring{N}_{\mathrm{gas}}} = \exp\left(\frac{-\mu_j(T_j^{\mathrm{kin}},p)}{kT_j^{\mathrm{kin}}}\right)\exp\left(\frac{-k(T_j^{\mathrm{kin}}-T_{\mathrm{gas}}) - \omega_j(T_j^{\mathrm{kin}},T_j^{\mathrm{int}}) - \lambda j}{kT_j^{\mathrm{kin}}}\right).$$

$$k_j^- = k_j^+\frac{\mathring{n}_A\mathring{n}_B}{\mathring{n}_{A+B}}$$

$$k^- = \frac{k^+p^{\ominus}}{kT_{\mathrm{gas}}}\exp\left(\sum_{i\in\zeta}\frac{\delta(i)}{kT_i^{\mathrm{kin}}}\left[\mu_i^{\ominus}(T_i^{\mathrm{kin}}) - i\mu_1^{\ominus}(T_{\mathrm{gas}}) + k(T_i^{\mathrm{kin}} - T_{\mathrm{gas}}) + \omega_i(T_i^{\mathrm{kin}},T_i^{\mathrm{int}})\right]\right)\left(\frac{kT_{\mathrm{gas}}\mathring{n}_1}{p^{\ominus}}\right)^{-\sum_{i\in\zeta}\delta(i)iT_{\mathrm{gas}}/T_i^{\mathrm{kin}}}$$

Maxwell-Boltzmann

$$M_T \equiv \frac{m_1}{T_1^{\text{kin}}} + \frac{m_2}{T_2^{\text{kin}}} = \frac{m_1 T_2^{\text{kin}} + m_2 T_1^{\text{kin}}}{T_1^{\text{kin}} T_2^{\text{kin}}}$$

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2}$$

$$\mu_T \equiv \frac{\frac{m_1}{T_1^{\text{kin}}}\frac{m_2}{T_2^{\text{kin}}}}{\frac{m_1}{T_1^{\text{kin}}} + \frac{m_2}{T_2^{\text{kin}}}} = \frac{m_1 m_2}{m_1 T_2^{\text{kin}} + m_2 T_1^{\text{kin}}}$$

$$\boldsymbol{v}_r \equiv \boldsymbol{v}_1 - \boldsymbol{v}_2$$

$$\boldsymbol{v}_T \equiv \frac{\frac{m_1}{T_1^{\text{kin}}}\boldsymbol{v}_1 + \frac{m_2}{T_2^{\text{kin}}}\boldsymbol{v}_2}{\frac{m_1}{T_1^{\text{kin}}} + \frac{m_2}{T_2^{\text{kin}}}} = \frac{m_1 T_2^{\text{kin}}\boldsymbol{v}_1 + m_2 T_1^{\text{kin}}\boldsymbol{v}_2}{m_1 T_2^{\text{kin}} + m_2 T_1^{\text{kin}}}$$

→

$$\int_{\mathbb{R}^3} f_r(\boldsymbol{v}_r) d\boldsymbol{v}_r = \int_{\mathbb{R}^3} f(\boldsymbol{v}_1) d\boldsymbol{v}_1 \int_{\mathbb{R}^3} f(\boldsymbol{v}_2) d\boldsymbol{v}_2$$
$$= \left(\frac{1}{2\pi k}\right)^3 \left(\frac{m_1 m_2}{T_1^{\text{kin}} T_2^{\text{kin}}}\right)^{3/2} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \exp\left(-\frac{M_T \boldsymbol{v}_T^2 + \mu_T \boldsymbol{v}_r^2}{2k}\right) d\boldsymbol{v}_r d\boldsymbol{v}_T$$
$$= \int_{\mathbb{R}^3} \left(\frac{\mu_T}{2\pi k}\right)^{3/2} \exp\left(-\frac{\mu_T \boldsymbol{v}_r^2}{2k}\right) d\boldsymbol{v}_r.$$

→

$$f_r(v_r) dv_r = \left(\frac{\mu_T}{2\pi k}\right)^{3/2} 4\pi v_r^2 \exp\left(-\frac{\mu_T v_r^2}{2k}\right) dv_r$$

↓

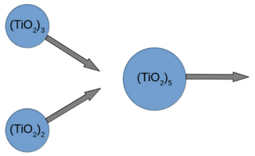
$$\frac{m_1}{T_1^{\text{kin}}}\boldsymbol{v}_1^2 + \frac{m_2}{T_2^{\text{kin}}}\boldsymbol{v}_2^2 = M_T \boldsymbol{v}_T^2 + \mu_T \boldsymbol{v}_r^2$$

↓

$$k_j^+ = \int_0^\infty \pi (r_1 + r_2)^2 v_r \left(\frac{\mu_T}{2\pi k}\right)^{3/2} 4\pi v_r^2 \exp\left(-\frac{\mu_T v_r^2}{2k}\right) dv_r = \pi (r_1 + r_2)^2 \sqrt{\frac{8k}{\pi \mu_T}}$$

- → Temperature-weighted reduced mass μ_T
- → In thermal equilibrium $\mu_T = \mu / T$

Inelastic collisions



$$\tilde{\boldsymbol{v}} \equiv \frac{m_1}{m_1+m_2}\boldsymbol{v}_1 + \frac{m_2}{m_1+m_2}\boldsymbol{v}_2$$

$$\tilde{\boldsymbol{v}}_T \equiv \frac{\frac{m_2}{T_1^{\mathrm{kin}}} m_1 \boldsymbol{v}_1 - \frac{m_1}{T_2^{\mathrm{kin}}} m_2 \boldsymbol{v}_2}{\frac{m_2}{T_1^{\mathrm{kin}}} + \frac{m_1}{T_2^{\mathrm{kin}}}}$$

$$\tilde{\mu} \equiv \frac{(m_1+m_2)^2}{m_1 T_1^{\mathrm{kin}} + m_2 T_2^{\mathrm{kin}}}$$

$$\tilde{M} \equiv \frac{\frac{m_2}{T_1^{\mathrm{kin}}} + \frac{m_1}{T_2^{\mathrm{kin}}}}{m_1 m_2}$$

$$\frac{m_1}{T_1^{\mathrm{kin}}}\boldsymbol{v}_1^2 + \frac{m_2}{T_2^{\mathrm{kin}}}\boldsymbol{v}_2^2 = \tilde{M}\tilde{\boldsymbol{v}}_T^2 + \tilde{\mu}\tilde{\boldsymbol{v}}^2$$

$$d\boldsymbol{v}_1 d\boldsymbol{v}_2 = \frac{1}{\mu^3} d\tilde{\boldsymbol{v}}_T d\tilde{\boldsymbol{v}}.$$

$$\iint_{\mathbb{R}^3} \mathrm{f}(\tilde{\boldsymbol{v}})d\tilde{\boldsymbol{v}} = \iint_{\mathbb{R}^3} f(\boldsymbol{v}_1)f(\boldsymbol{v}_2)d\boldsymbol{v}_1 d\boldsymbol{v}_2$$
$$= \iint_{\mathbb{R}^3} \left(\frac{1}{2\pi k}\right)^3 \left(\frac{m_1 m_2}{T_1 T_2}\right)^{3/2} \exp\left(-\frac{\tilde{M}\tilde{\boldsymbol{v}}_T^2 + \tilde{\mu}\tilde{\boldsymbol{v}}^2}{2k}\right)\frac{1}{\mu^3} d\tilde{\boldsymbol{v}}_T d\tilde{\boldsymbol{v}}$$
$$= \int_{\mathbb{R}^3} \left(\frac{\tilde{\mu}}{2\pi k}\right)^{3/2} \exp\left(-\frac{\tilde{\mu}\tilde{\boldsymbol{v}}^2}{2k}\right) d\tilde{\boldsymbol{v}}$$

$$T^{\mathrm{kin}} = \frac{(m_1+m_2)}{\tilde{\mu}} = \frac{m_1 T_1^{\mathrm{kin}} + m_2 T_2^{\mathrm{kin}}}{(m_1+m_2)} = T_1^{\mathrm{kin}} + T_2^{\mathrm{kin}} - \frac{\mu}{\mu_T}$$

$$\Delta T_{\mathrm{inel}}^{\mathrm{int}} = \frac{2}{D_f k}\left(\Delta E_{\mathrm{inel}}^{\mathrm{kin}} + \Delta E_{\mathrm{frebind}}\right) = \frac{2}{D_f k}\left(\frac{3k\mu}{2\mu_T} + \Delta E_{\mathrm{bind}}\right)$$

$$(m_1+m_2)\,\tilde{\boldsymbol{v}} = m_1\,\boldsymbol{v}_1 + m_2\,\boldsymbol{v}_2$$

Time dependency

$$T_i(\Delta t) = T_{\text{gas}} + T_{i,0} \exp(-\Delta t/\tau_i)$$

$$k_j^+(\Delta t_1, \Delta t_2) = \pi(r_1 + r_2)^2 \sqrt{\frac{8k}{\pi m_1 m_2}(m_2 T_1^{\text{kin}}(\Delta t_1) + m_1 T_2^{\text{kin}}(\Delta t_2))}$$

$$P_i(\Delta t) = (\tau_i)^{-1} \exp(-\Delta t/\tau_i)$$

$$\tilde{k}_j^+ = \int_0^\infty \int_0^\infty P_1(\Delta t_1) P_2(\Delta t_2)\, k_j^+(\Delta t_1, \Delta t_2)\, d(\Delta t_1)\, d(\Delta t_2)$$

$$\tau_{A,j}^{\text{coll},+} = \frac{1}{n_B k_j^+}$$

$$\tau_{A,j}^{\text{coll},+} = \tau_{\text{gc}}^{\text{kin}}$$

$$\epsilon_B = \frac{8}{3} \frac{r_B^2}{(r_A + r_B)^2} \sqrt{\frac{m_{\text{gas}} m_B T_{\text{gas}}}{m_A(m_A T_B + m_B T_A)}}$$

$$\epsilon_{(\text{TiO}_2)_2} = 0.053 \sqrt{\frac{T_{\text{gas}}}{T^{\text{kin}}_{(\text{TiO}_2)_2}}}$$