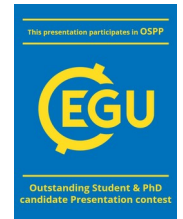# The effect of thermal non-equilibrium on aerosol formation in astrophysical environments

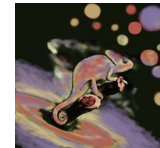## Sven Kiefer

David Gobrecht, Leen Decin, Christiane Helling

Overview
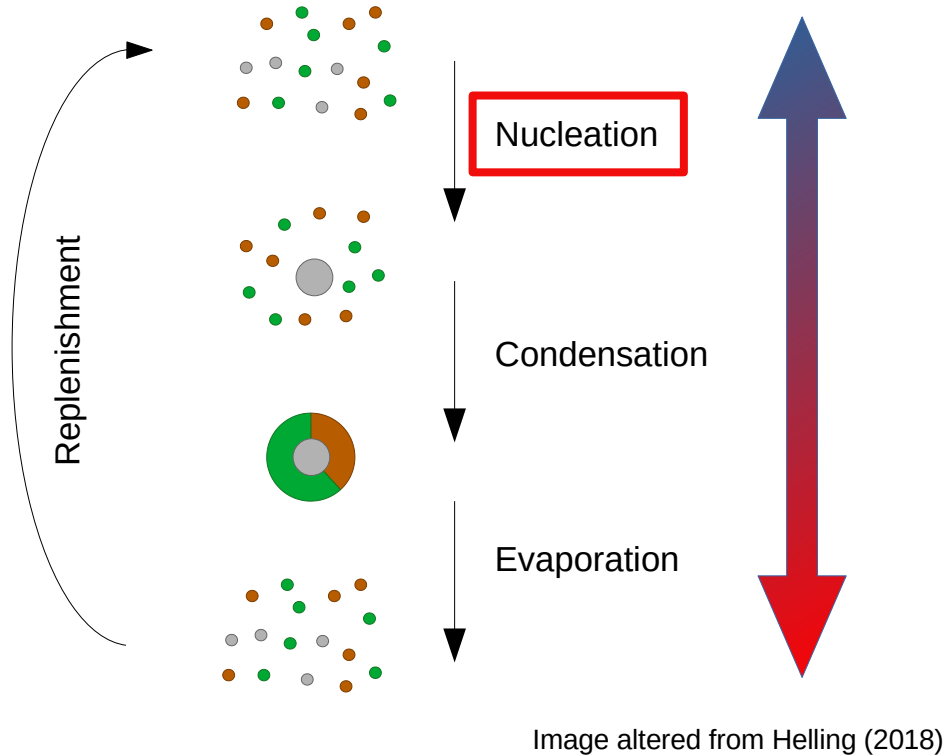

Nucleation

Condensation

Evaporation

Replenishment

Image altered from Helling (2018)

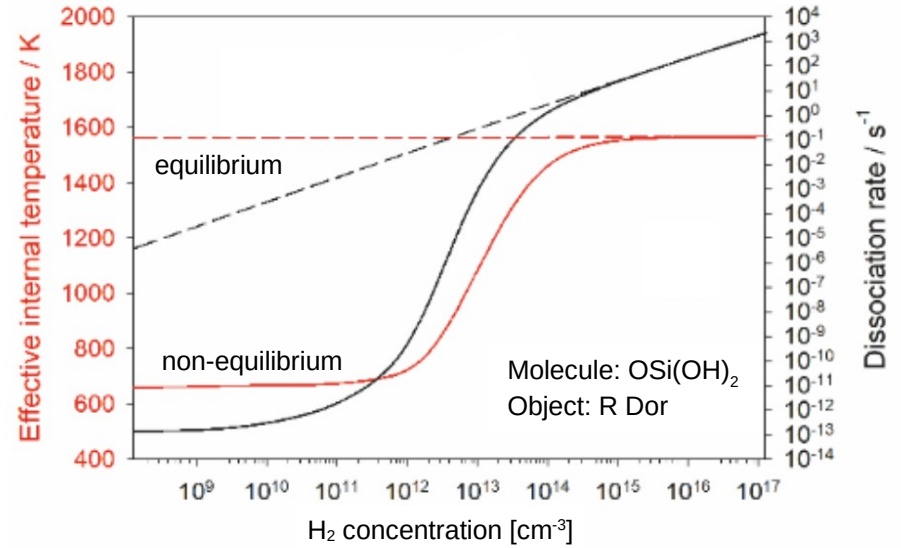Plane and Robertson (2022):

Molecule: $OSi(OH)_2$
Object: R Dor

Image altered from
Plane and Robertson (2022)

Observational evidence:
• Fonfría et al. 2008, 2017, 2021

The effect of thermal non-equilibrium

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Kiefersv.github.io
@ExoSvenK

- Nucleation is sensitive to thermal non-equilibrium

- The type of thermal non-equilibrium present matters

- $\Delta T < 0$ can increase and $\Delta T > 0$ can decrease the amount of clusters

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

The effect of thermal non-equilibrium on aerosol formation in astrophysical environments

Sven Kiefer[1,2,3,4], David Gobrecht[1], Leen Decin[1], Christiane Helling[2,3,4]

Explore our work

Here you can get a small guided tour through the theory behind kinetic nucleation, how thermal non-equilibrium can be described and our results.

Kinetic nucleation theory

Learn how the formation of clusters can be described fully kinetically

Thermal non-equilibrium

Learn where we can observe thermal non-equilibrium and how models describe it.

Results

Check out our results and how we expect thermal non-equilibrium to affect the formation of aerosols.

30 second summary

Cloud formation happens when gas phase species condense onto aerosols. The formation of aerosols, called nucleation, is the transition from gas phase chemistry to solid chemistry.
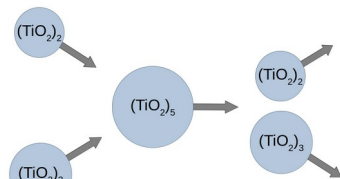
In this work, we study the impact of thermal non-equilibrium on the kinetic description of nucleation.
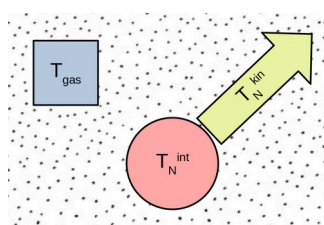
Thermal non-equilibrium can be caused by, for example, radiative cooling in low density environments. In our work, we consider that the gas phase temperature and the kinetic and internal temperature of each cluster size can be different.

Results:

- Nucleation is sensitive to thermal non-equilibrium

- The type of thermal non-equilibrium present matters

- $\Delta T < 0$ can increase and $\Delta T > 0$ can decrease the amount of clusters
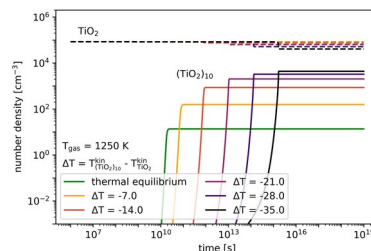
Additional material

Cooling timescales

Learn more about the most important cooling and heating processes of clusters.

Mathematical derivation

Our work dives deep into thermodynamics. Here you can be guided through the core derivations of our work.

Re-visit the presentation

Did you miss something during the 2-minute PICO presentation? Look it up here!

About me

Sven Kiefer
Kiefersv.github.io
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Read the paper:
"The effect of thermal non-equilibrium on kinetic nucleation"

EGU:

Affiliations

1) Institute of Astronomy, KU Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium
2) Centre for Exoplanet Science, University of St Andrews, North Haugh, St Andrews, KY169SS, UK
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The effect of thermal non-equilibrium on aerosol formation in astrophysical environments

Sven Kiefer

David Gobrecht, Leen Decin, Christiane Helling

Overview

Nucleation

Condensation

Evaporation

Replenishment

Image altered from Helling (2018)

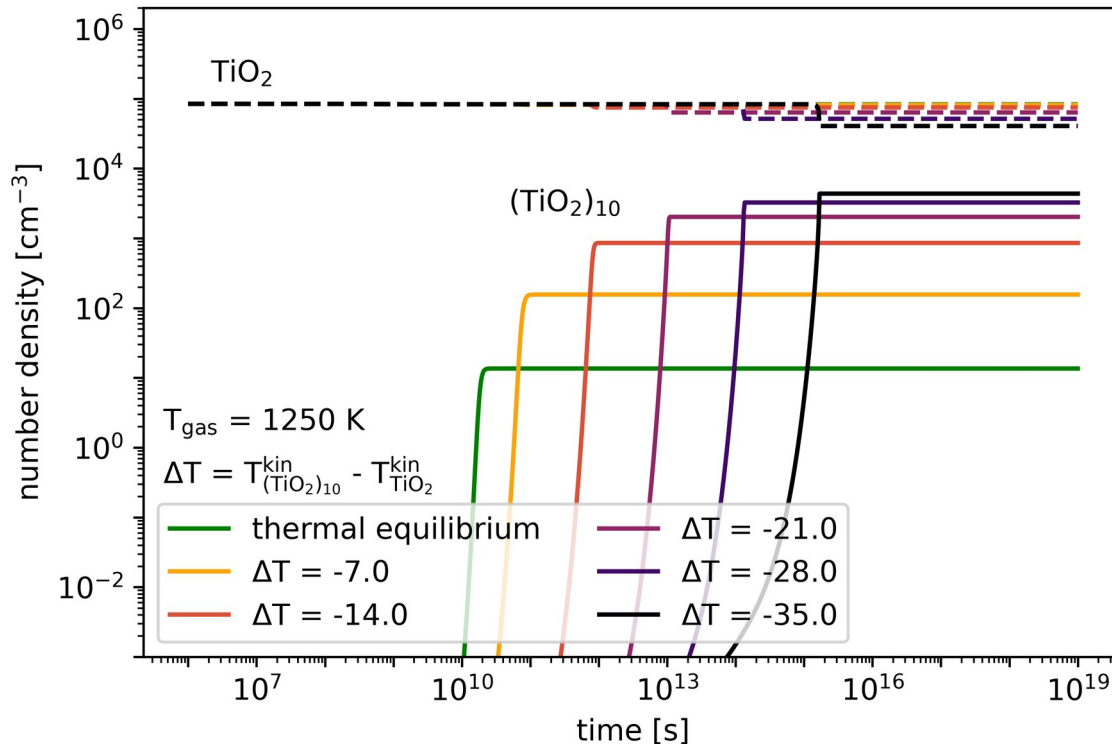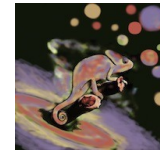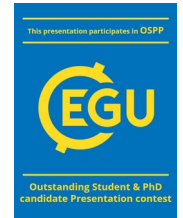Plane and Robertson (2022):

Molecule: OSi(OH)$_2$
Object: R Dor

Image altered from
Plane and Robertson (2022)

Observational evidence:
- Fonfría et al. 2008, 2017, 2021

The effect of thermal non-equilibrium

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- Nucleation is sensitive to thermal non-equilibrium

- The type of thermal non-equilibrium present matters

- $\Delta T < 0$ can increase and $\Delta T > 0$ can decrease the amount of clusters

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

HOME

$(TiO_2)_2$

$(TiO_2)_3$

$(TiO_2)_5$

Nucleation describes the change from the gas phase to the solid. Here we will show how we describe the first steps of this transition.

Press the arrow to go to the next step!

Kinetic nucleation theory

Sven Kiefer - EGU

HOME

$(TiO_2)_2$

$(TiO_2)_3$

$(TiO_2)_5$
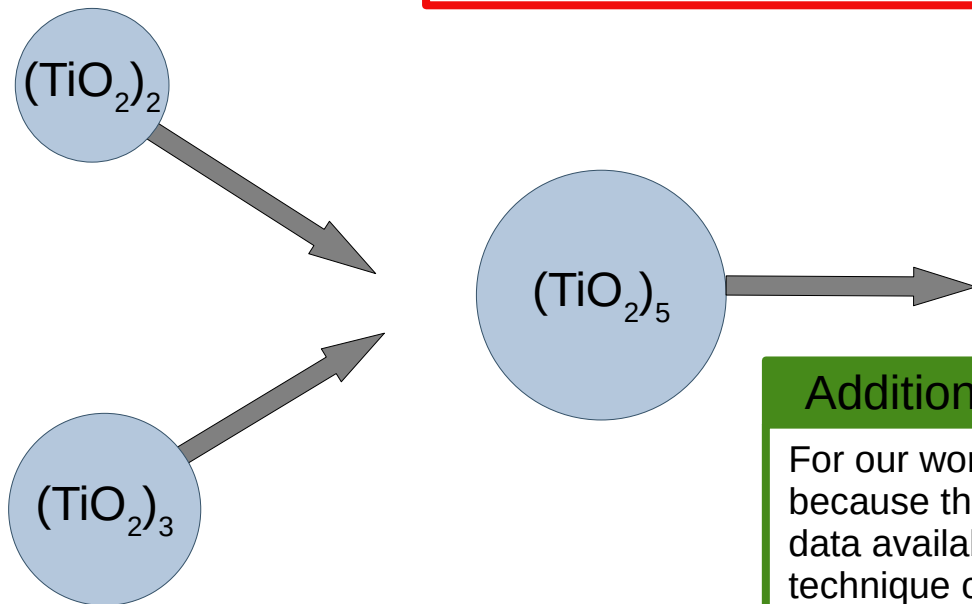
Theory

In kinetic nucleation theory, the growth of clusters is described via collisions of smaller clusters resulting into a lager cluster.

Additional

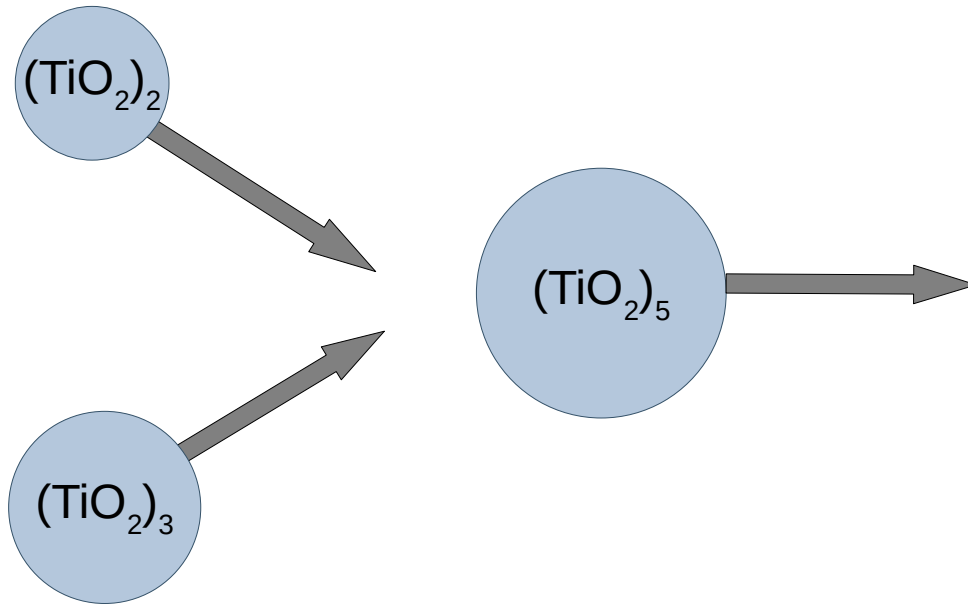Similar to kinetic nucleation, the chemistry of the gas phase can also be described kinetically. This is commonly done to model the abundances of gas phase species in environments where chemical disequilibrium is expected.

An important difference to the chemistry description is that the product of a cluster growth reaction has 1 product whereas chemistry often has 2.

Additional

For our work we looked at TiO_2 because there is detailed cluster data available. The same technique can be applied to any nucleating species.

Kinetic nucleation theory

σ

(TiO$_2$)$_2$

(TiO$_2$)$_3$

(TiO$_2$)$_5$

The growth rate, or forward rate, depends on the cross section of the colliding clusters ….
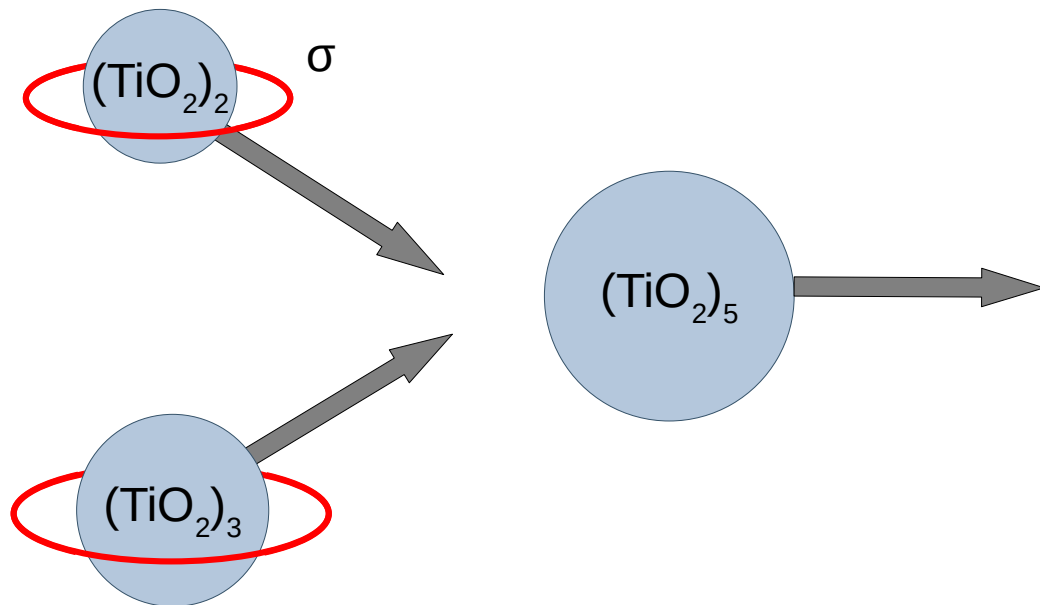
Additional

For the calculation of the cross section we considered not only the geometric cross section but also the Coulomb potential.

Theory

…. the relative velocity between the clusters ….

$(TiO_2)_2$ σ

ν_r

$(TiO_2)_3$

$(TiO_2)_5$
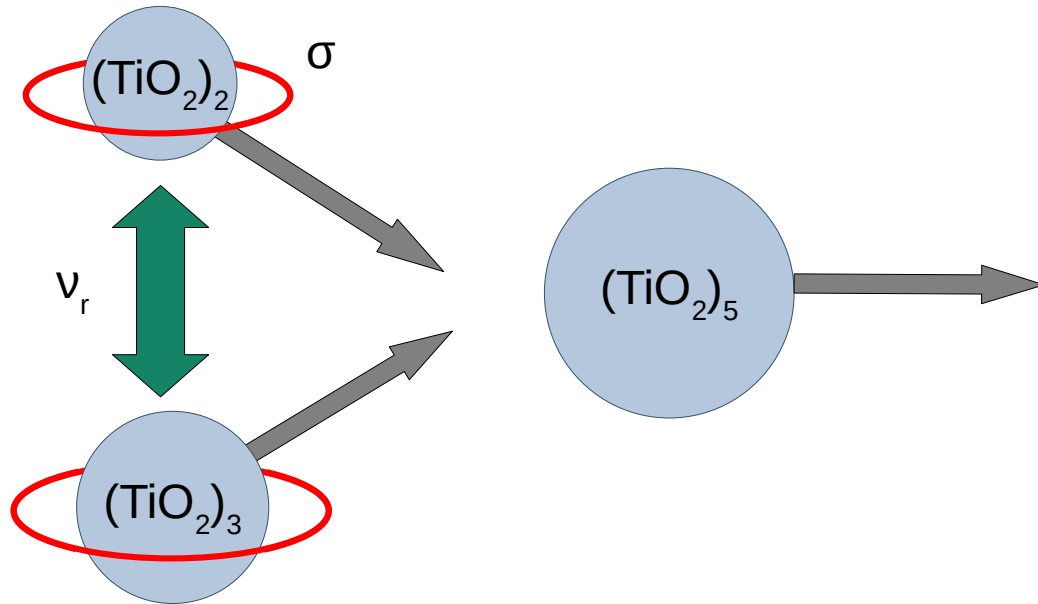
Additional

The relative velocity is given by a Maxwell-Boltzmann distribution:

$$f(\boldsymbol{v})d\boldsymbol{v} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m\boldsymbol{v}^2}{2kT}\right)d\boldsymbol{v}$$

HOME

Theory

…. and the probability that a collision results in a bigger cluster, given by the sticking coefficient.

σ

$(TiO_2)_2$

ν_r

$(TiO_2)_3$

α

$(TiO_2)_5$
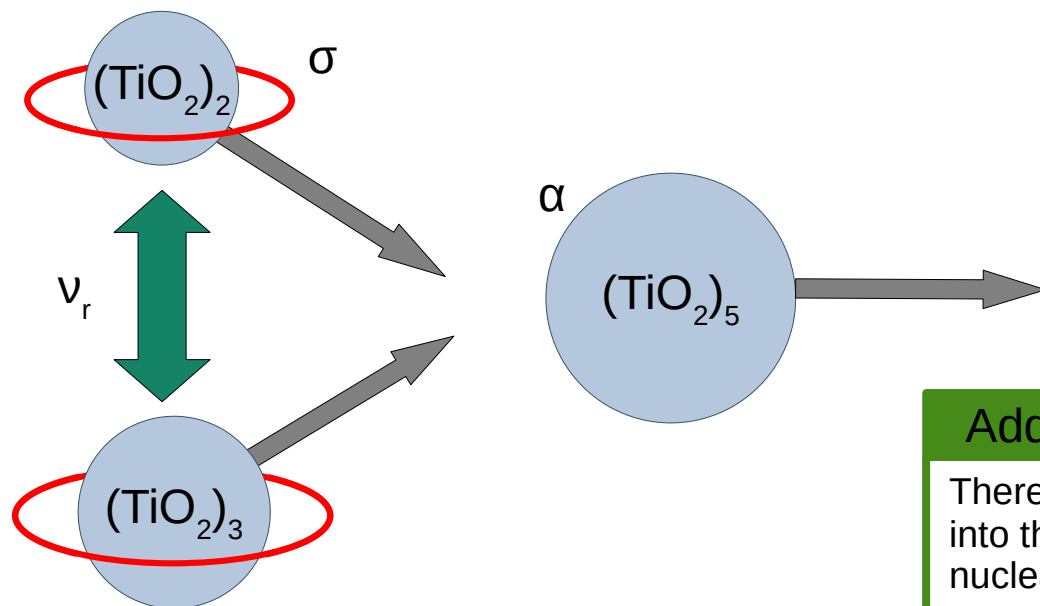
Additional

There are only few studies looking into the sticking coefficients of nucleation reactions. For this study we assume a coefficient of 1.

$$(TiO_2)_2$$

σ

$$\nu_r$$

$$(TiO_2)_3$$

α

$$(TiO_2)_5$$
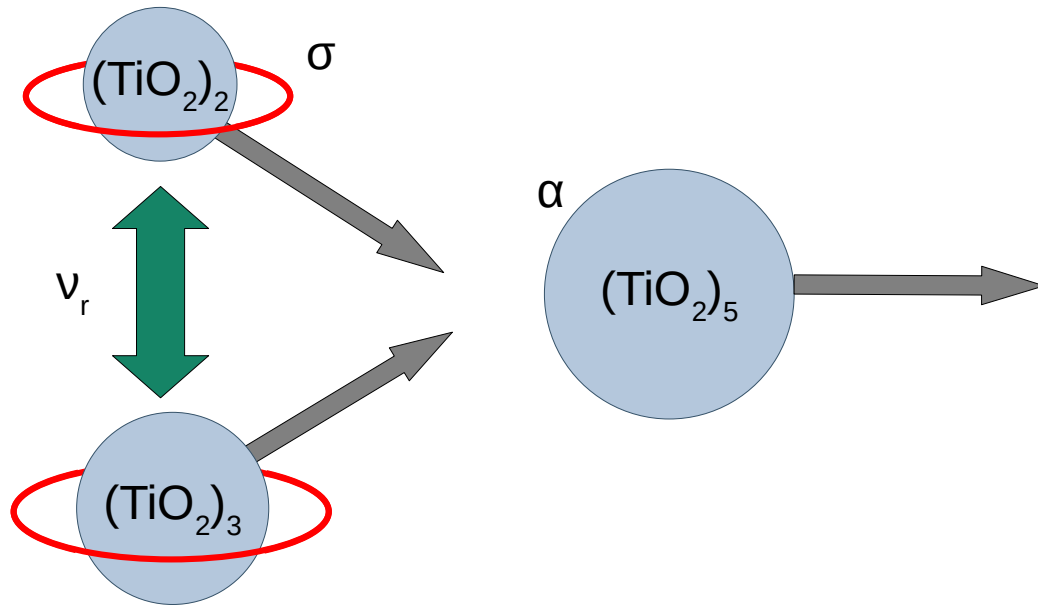
Integrating over the relative velocity distribution gives us the forward reaction rate.

$$k^+ = \int_0^\infty \alpha(v_r)\, \sigma(v_r)\, v_r\, f(v_r)\, dv_r$$

Kinetic nucleation theory

Sven Kiefer - EGU

The backward rate describes the dissociation of a large cluster into two smaller clusters.

$(TiO_2)_2$

$(TiO_2)_5$

$(TiO_2)_3$

(TiO$_2$)$_5$

(TiO$_2$)$_2$

(TiO$_2$)$_3$
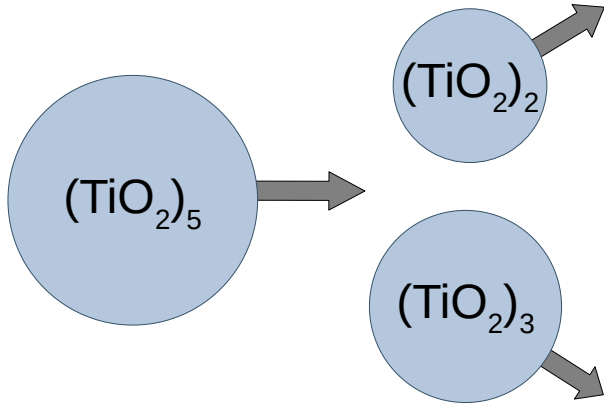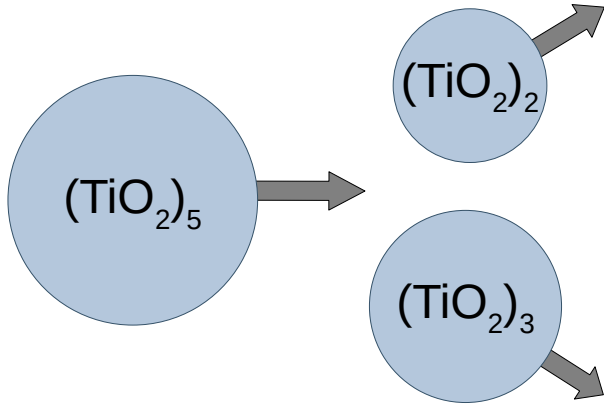
Theory

In chemical equilibrium, the number of forward reactions equals the number of backward reactions. Therefore we can find the relation between the two as:

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

Additional

This principal is called detailed balance and is also often used to find backward rate of gas phase chemical reactions.
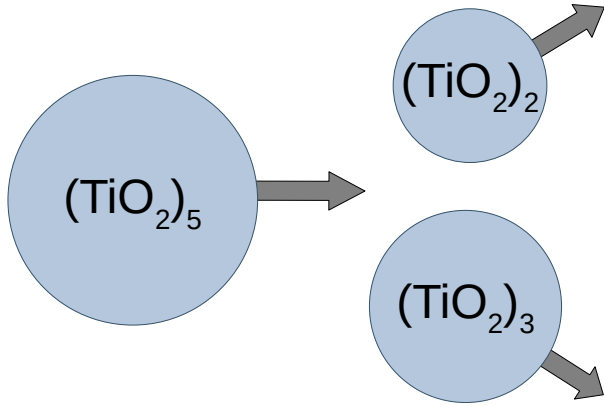
The law of mass action is derived by minimizing the total Gibbs free energy of the gas and therefore maximizes the entropy.

$(TiO_2)_5$

$(TiO_2)_2$

$(TiO_2)_3$

Detailed balance:

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

Theory

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

The ratio between the number densities of the products and reactants in equilibrium is given by the law of mass action.

$(TiO_2)_5$

$(TiO_2)_2$

$(TiO_2)_3$

Detailed balance:

$$\frac{k_{N,M}^-}{k_{N,M}^+} = \frac{n_N^{eq} n_M^{eq}}{n_{N+M}^{eq}}$$

Law of mass action:

$$\frac{n_N^{eq} n_M^{eq}}{n_{N+M}^{eq}} = \frac{P^\circ}{k_B T} \exp\left(\frac{G_{N+M}^\circ - G_M^\circ - G_N^\circ}{k_B T}\right)$$

Theory

$$k_{N,M}^- = k_{N,M}^+ \frac{P^\circ}{k_B T} \exp\left(\frac{G_{N+M}^\circ - G_M^\circ - G_N^\circ}{k_B T}\right)$$

Combining both gives us the backward reaction rate.
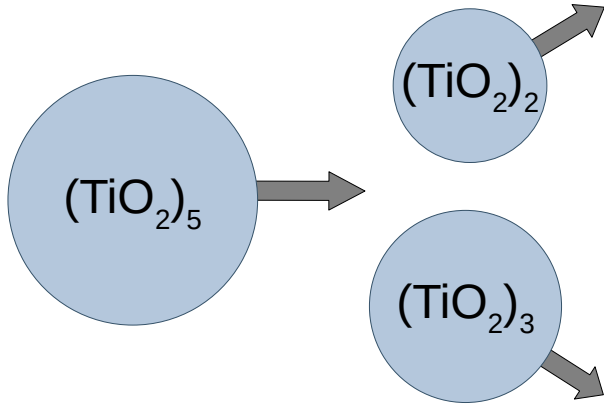
Detailed balance:

$$\frac{k_{N,M}^-}{k_{N,M}^+} = \frac{n_N^{\text{eq}} n_M^{\text{eq}}}{n_{N+M}^{\text{eq}}}$$

Law of mass action:
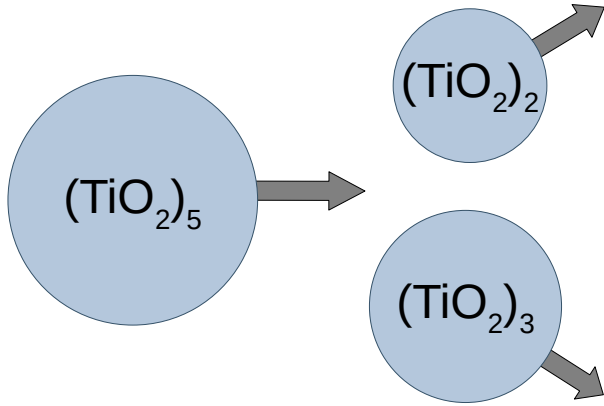
$$\frac{n_N^{\text{eq}} n_M^{\text{eq}}}{n_{N+M}^{\text{eq}}} = \frac{P^\circ}{k_{\text{B}}T} \exp\left(\frac{G_{N+M}^\circ - G_M^\circ - G_N^\circ}{k_{\text{B}}T}\right)$$

$$k_{N,M}^- = k_{N,M}^+ \frac{P^\circ}{k_{\text{B}}T} \exp\left(\frac{G_{N+M}^\circ - G_M^\circ - G_N^\circ}{k_{\text{B}}T}\right)$$

Continue and learn about how thermal non-equilibrium affects the forward and backward rate.

Kinetic nucleation theory

Sven Kiefer - EGU

HOME

T_{gas}

T_N^{kin}

T_N^{int}
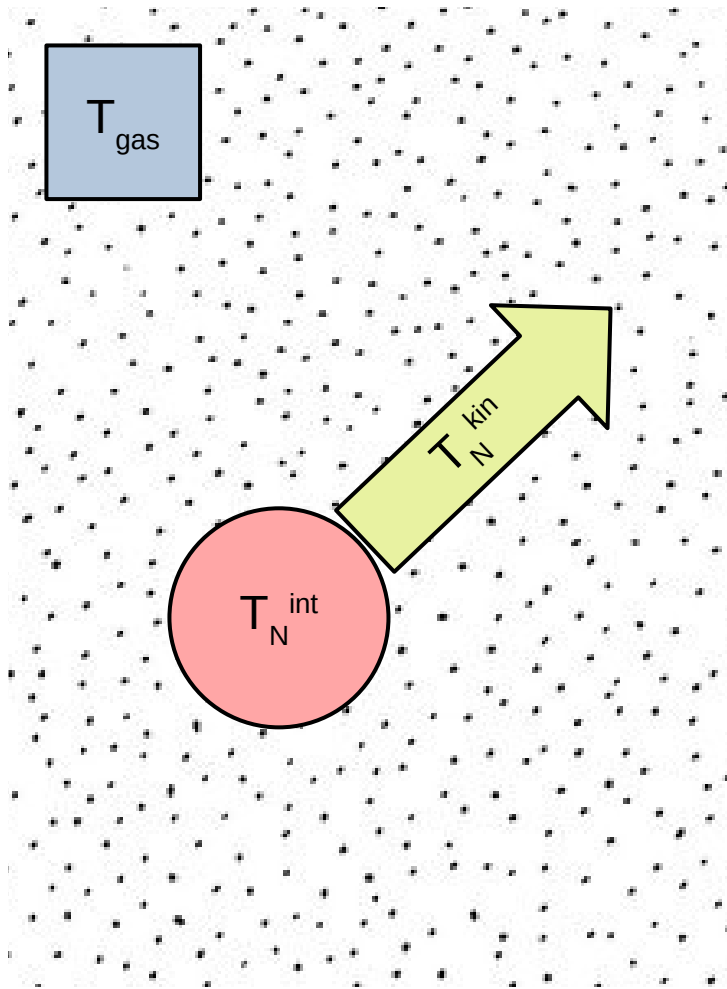
Thermal non-equilibrium means that not all particles are at the same temperature. Here, we explain how we and others describe these temperature differences and what effects they have on kinetic nucleation.

Press the arrow to go to the next step!
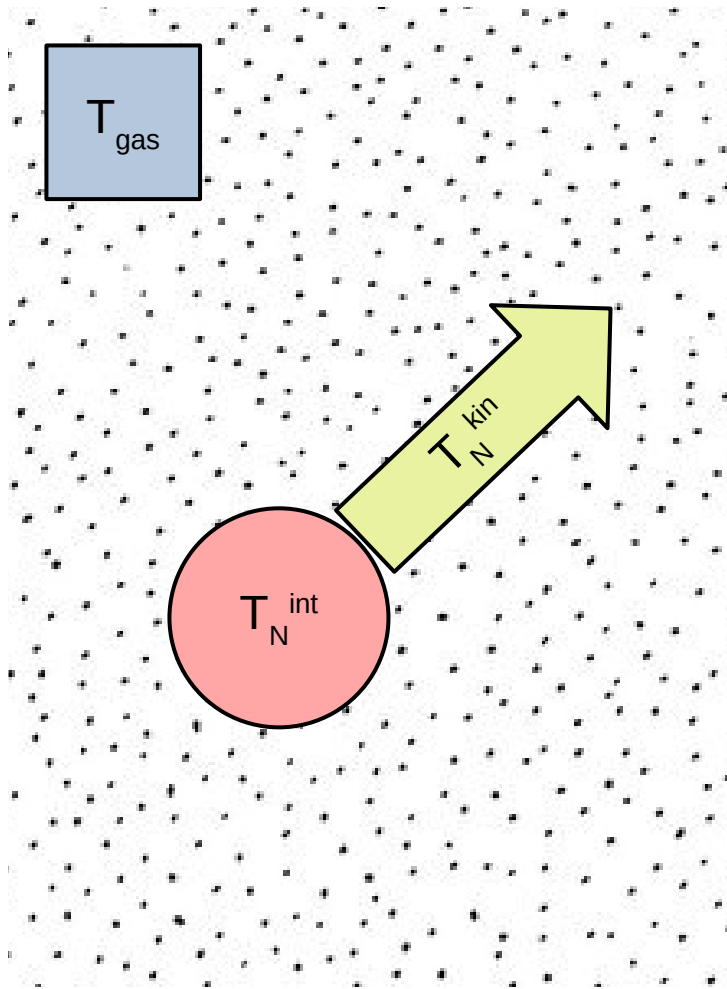
T_{gas}

T_N^{kin}

T_N^{int}

Theory

In our work, we assume the gas phase to be in thermal equilibrium. Each cluster size on the other hand can have a different internal and kinetic temperature:

$$T_{gas} \neq T_N^{kin} \neq T_N^{int}$$

Additional

In our work, the internal and kinetic temperature are defined over the energy in the translational degrees of freedom (kinetic) and the vibrational/rotational degrees of freedom (internal):

$$E_N^{tot} = E_N^{kin} + E_N^{int} = \frac{3}{2}kT_N^{kin} + \frac{D_N^f}{2}kT_N^{int}$$

Where D_n^f is the number of internal + rotational degrees of freedom and k is the Boltzmann constant.
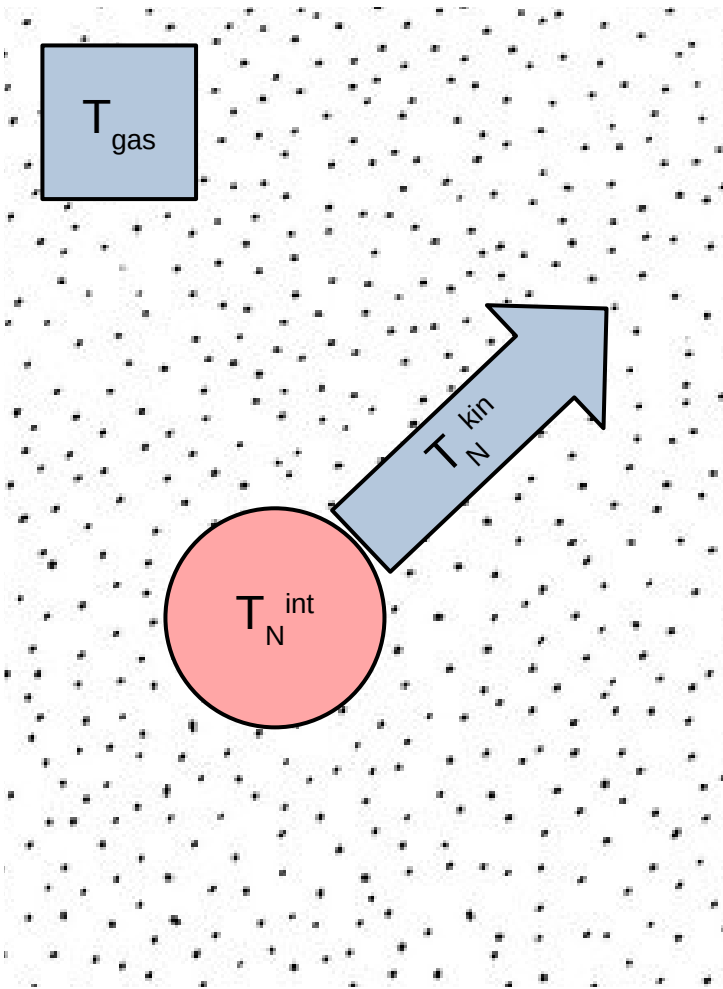
Theory

Plane and Robertson (2022) did a detailed analysis of internal cooling via optical lines of $OSI(OH)_2$:

$$T_{gas} = T_N^{kin} \neq T_N^{int}$$

Our work

$$T_{gas} \neq T_N^{kin} \neq T_N^{int}$$

Additional

In their work, Plane and Robertson (2022) looked at 11 optical lines and derived a master equation which describes the internal temperature of $OSI(OH)_2$ and its disassociation rate in detail. They found that thermal non-equilibrium can be present in low density environments, and that it can cause significant changes in the disassociation rate of $OSI(OH)_2$.

T_{gas}

T_N^{kin}

T_N^{int}
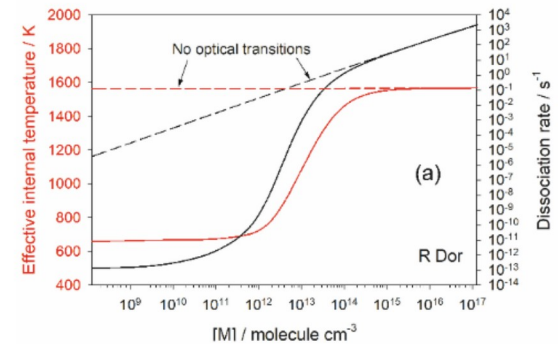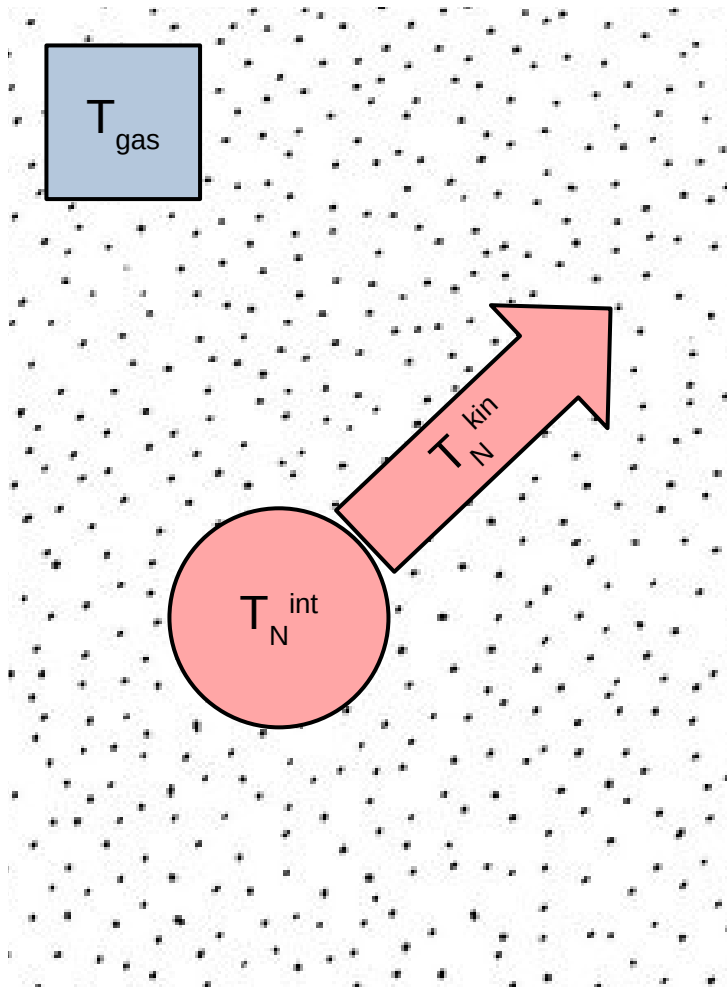
T_{gas}

T_N^{kin}

T_N^{int}

Theory

Other works (e.g. Patzer et al. 1998, Köhn et al. 2021) adopt a single temperature for each cluster size N:

$$T_{gas} \neq T_N^{kin} = T_N^{int}$$

Our work

$$T_{gas} \neq T_N^{kin} \neq T_N^{int}$$

Plane and Robertson (2022)

$$T_{gas} = T_N^{kin} \neq T_N^{int}$$

Thermal non-equilibrium — Sven Kiefer - EGU

Thermal non-equilibrium

Thermal equilibrium

$$k^+ = \int_0^\infty \alpha(v_r)\, \sigma(v_r)\, v_r\, f(v_r)\, dv_r$$

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

Thermal non-equilibrium

$$k^+ = \int_0^\infty \alpha(v_r)\, \sigma(v_r)\, v_r\, f(v_r)\, dv_r$$

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

$$A = \exp\left(\sum_{i \in \zeta} \frac{\delta(i)}{k T^{\text{kin}}_i} \left[G^\circ_i(T^{\text{kin}}_i) - i G^\circ_1(T^{\text{kin}}_i) + k(T^{\text{kin}}_i - T_{\text{gas}}) \right] \right)$$

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

$$C = \left(\frac{k T_{\text{gas}} n^{\text{eq}}_1}{p^\circ} \right)^{-\sum_{i \in \zeta} \delta(i) i \frac{T_{\text{gas}}}{T^{\text{kin}}_i}}$$

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

Thermal equilibrium

$$k^+ = \int_0^\infty \alpha(v_r)\, \sigma(v_r)\, v_r\, f(v_r)\, dv_r$$

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

Thermal non-equilibrium

$$k^+ = \int_0^\infty \alpha(v_r)\, \sigma(v_r)\, v_r\, f(v_r)\, dv_r$$

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

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

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

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

Additional

δ(i) is the sign for the sum over products and reactants where products have a positive sign and reactants have a negative sign.

Theory

The forward and backward rates in thermal non-equilibrium include all terms of the thermal equilibrium case. Both descriptions are equivalent in thermal equilibrium.

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

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

Thermal equilibrium

$$k^+ = \int_0^\infty \alpha(v_r)\, \sigma(v_r)\, v_r\, f(v_r)\, dv_r$$

$$k_{N,M}^- = k_{N,M}^+ \frac{P^\circ}{k_\mathrm{B}T} \exp\left(\frac{G_{N+M}^\circ - G_M^\circ - G_N^\circ}{k_\mathrm{B}T}\right)$$

Theory

The impact of different gas and kinetic temperatures is given by the red terms. In the forward rate, the sticking coefficient and cross section can be affected by thermal non-equilibrium but these effects are not considered in this study.

Thermal non-equilibrium

$$k^+ = \int_0^\infty \alpha(v_r)\, \sigma(v_r)\, v_r\, f(v_r)\, dv_r$$

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

$$A = \exp\left(\sum_{i \in \zeta} \frac{\delta(i)}{kT_i^{kin}}\left[G_i^\circ(T_i^{kin}) - iG_1^\circ(T_i^{kin}) + k(T_i^{kin} - T_{gas})\right]\right)$$

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

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

Thermal equilibrium

$$k^+ = \int_0^\infty \alpha(v_r)\,\sigma(v_r)\,v_r\,f(v_r)\,dv_r$$

$$k_{N,M}^- = k_{N,M}^+ \frac{P^\circ}{k_B T} \exp\left(\frac{G_{N+M}^\circ - G_M^\circ - G_N^\circ}{k_B T}\right)$$

Theory

The impact of different gas and kinetic temperatures is given by the green terms. The variable ω_i denotes the difference in Gibbs free energy of a cluster if the kinetic and internal temperature are different.

Thermal non-equilibrium

$$k^+ = \int_0^\infty \alpha(v_r)\,\sigma(v_r)\,v_r\,f(v_r)\,dv_r$$

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

$$A = \exp\left(\sum_{i\in\zeta} \frac{\delta(i)}{k T_i^{kin}}\Big[G_i^\circ(T_i^{kin}) - iG_1^\circ(T_i^{kin}) + k(T_i^{kin} - T_{gas})\Big]\right)$$

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

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

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

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

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

Gauge

Thermal equilibrium

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

$$k_{N,M}^- = k_{N,M}^+ \frac{P^\circ}{k_B T}\exp\left(\frac{G_{N+M}^\circ - G_M^\circ - G_N^\circ}{k_B T}\right)$$

Theory

The orange terms are gauge terms. They originate from the fact that the Gibbs free energy is a relative quantity and only the difference between different particles matters.

Thermal non-equilibrium

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

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

$$A = \exp\left(\sum_{i \in \zeta} \frac{\delta(i)}{kT_i^{kin}}\left[G_i^\circ(T_i^{kin}) - iG_1^\circ(T_i^{kin}) + k(T_i^{kin} - T_{gas})\right]\right)$$

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

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

Now that you know the theory, check out the results!
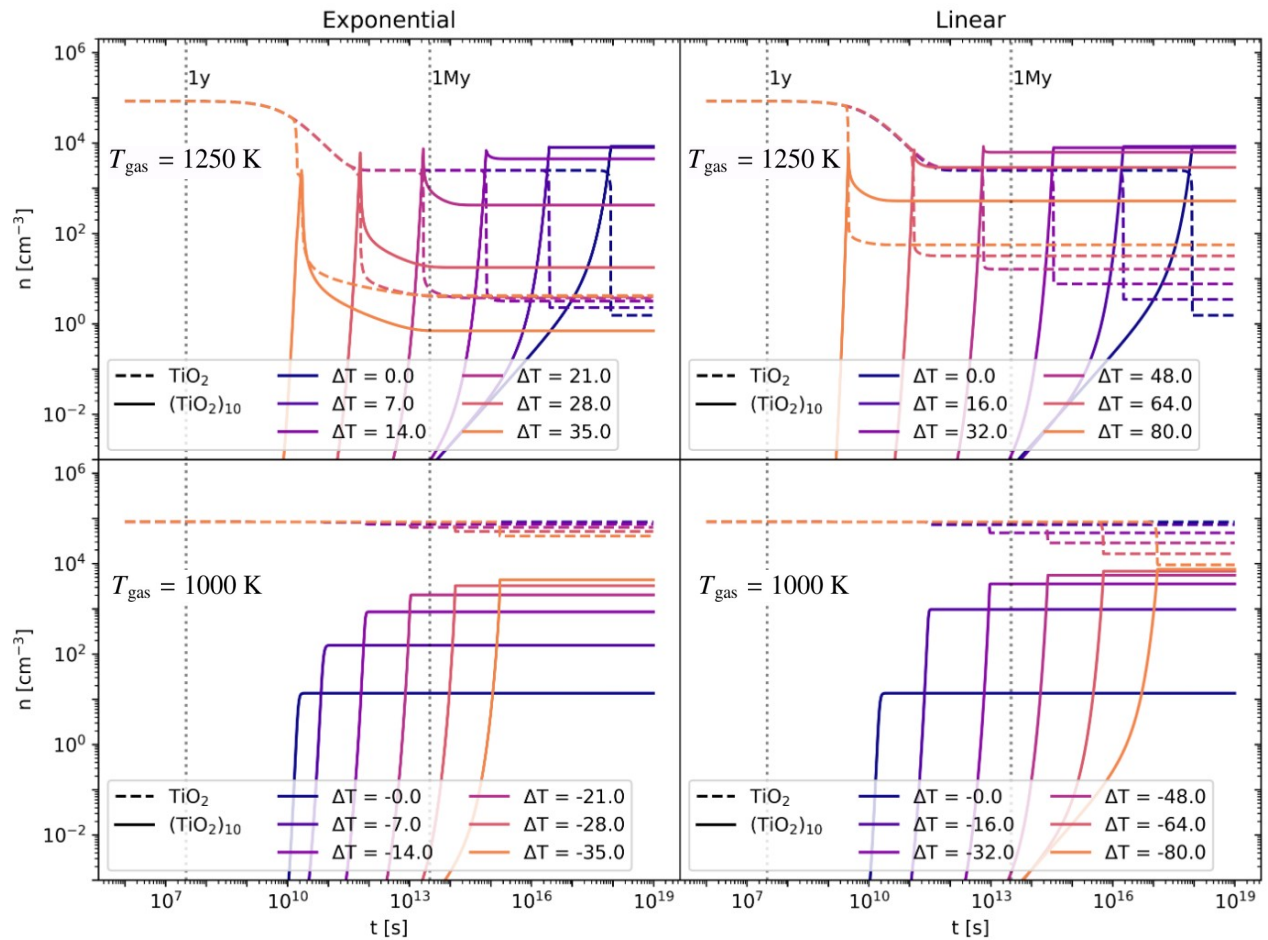
Thermal non-equilibrium affects the formation of aerosols. Here we elaborate on how the formation of larger clusters is affected.

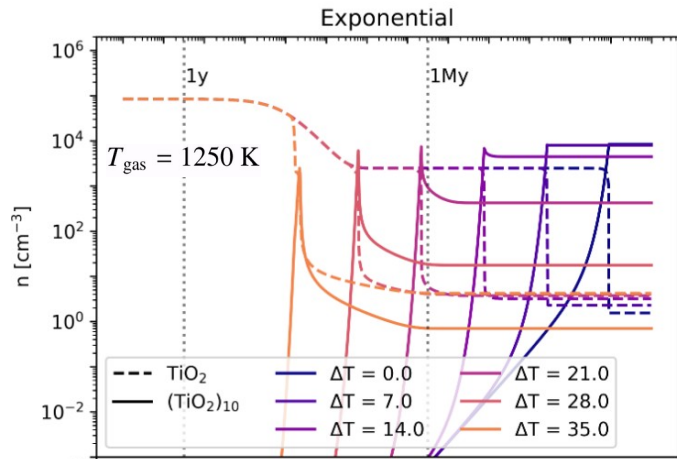Press the arrow to go to the next step!

Results

Sven Kiefer - EGU

HOME

Exponential

Theory

First, it is important to note, that small thermal non-equilibrium can have a strong effect on the occurrence of larger clusters.

Additional

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

ΔT denotes the temperature difference between the smallest and largest size.

Additional

Here we see that temperature differences of less then 35 K can already reduce the number density of our largest cluster $(\mathrm{TiO}_2)_{10}$ by several orders of magnitude. This is much larger than an equivalent temperature decrease in thermal equilibrium would cause.

Results   Sven Kiefer - EGU   HOME

Additional

$$\Delta T = T^{\text{kin}}_{(TiO_2)_{10}} - T^{\text{kin}}_{TiO_2}$$
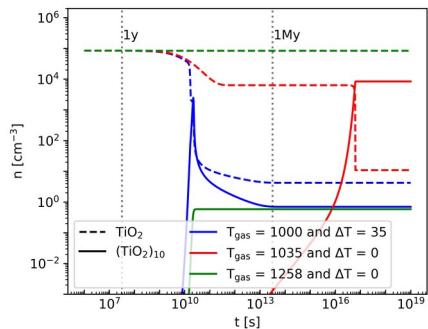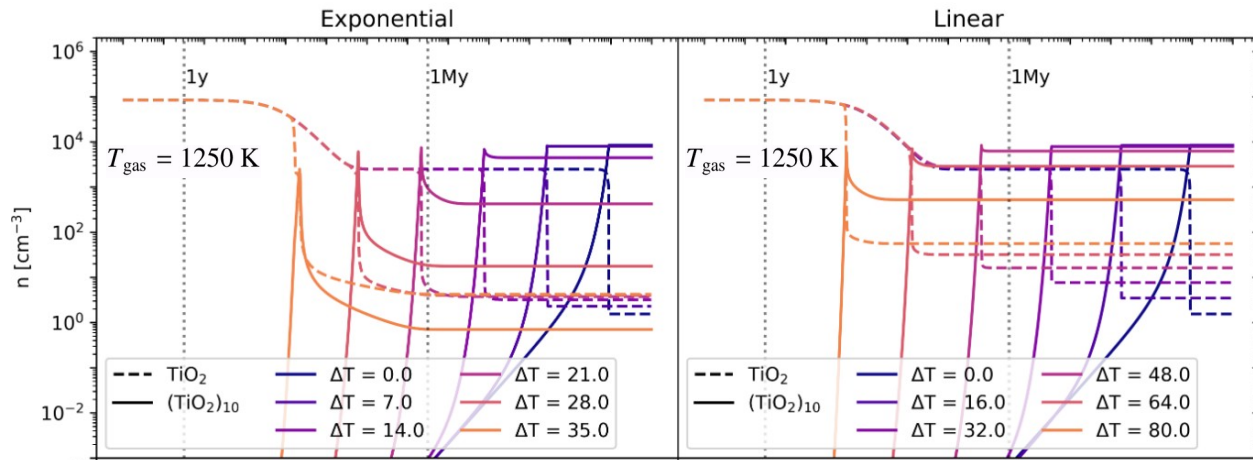
Linear: $\quad T^{\text{kin}}_N = T_{\text{gas}} + \dfrac{e^{N-1} - 1}{e^9 - 1}\Delta T$

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

For this work, we considered two different temperature steppings.

Theory

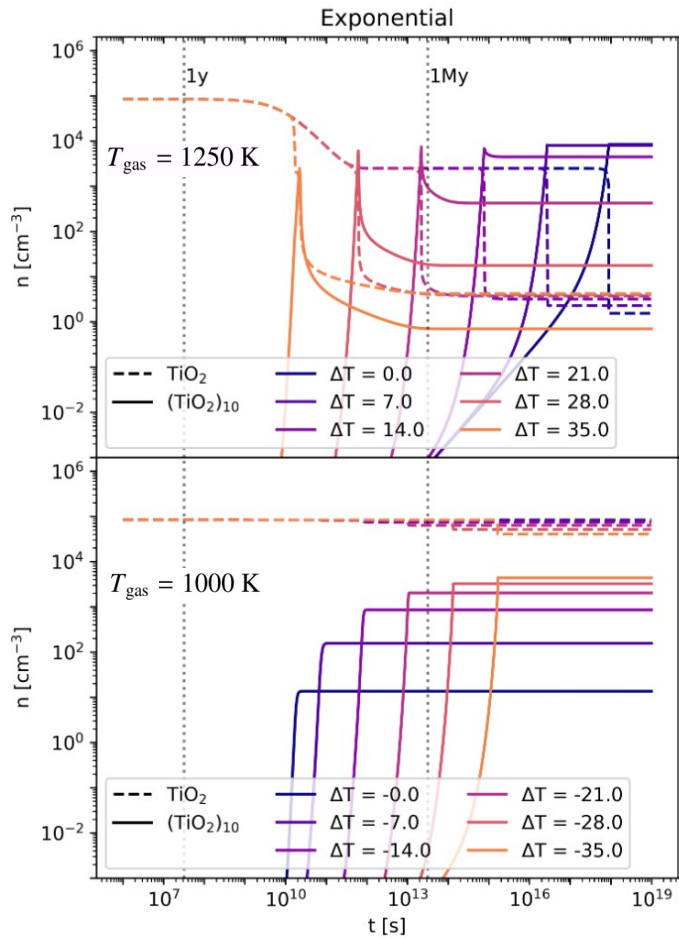Not only the temperature difference between the smallest and largest TiO_2 cluster matters but also the difference in cluster temperature between all clusters.

Exponential

If the formation of larger clusters is favored, increasing temperatures for larger clusters can inhibit the cluster formation. Vice versa, if the formation of larger clusters is disfavored, decreasing temperatures for larger clusters can increase the cluster formation

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

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

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

Additional

The examples chosen for this work were set up specifically to showcase the effect that thermal non-equilibrium can have. Other cases (like decreasing temperatures for larger clusters in an environment already favoring larger clusters) need to be studied on a case by case basis. Generally, our simulations showed the strongest impact of thermal non-equilibrium in temperature ranges where the number density of large clusters already showed a strong temperature dependence (e.g. around 1000 K - 1300 K for TiO_2).

Results

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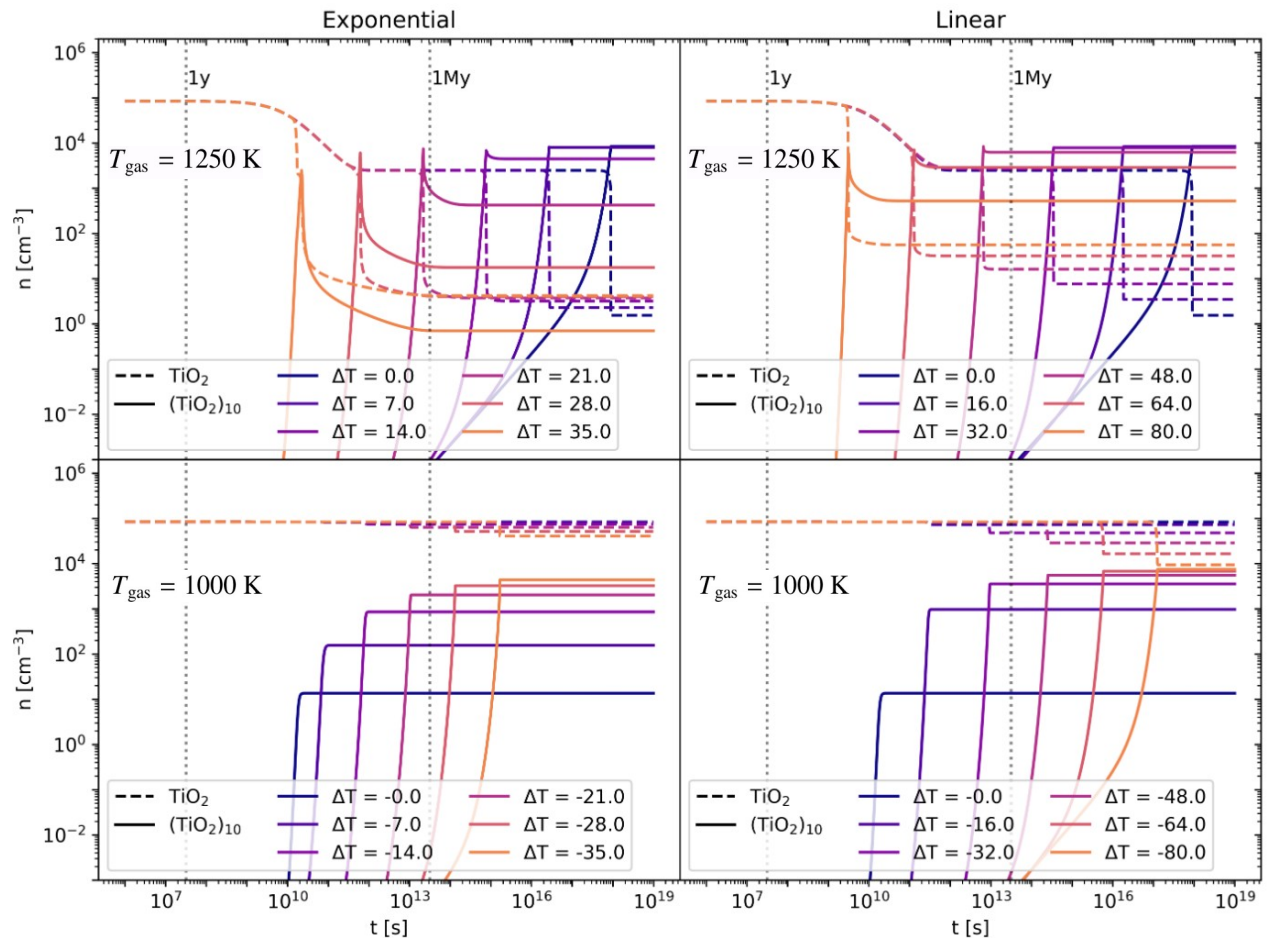$$\Delta T = T^{\text{kin}}_{(\text{TiO}_2)_{10}} - T^{\text{kin}}_{\text{TiO}_2}$$

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

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

Theory

To Summarize:

- Small temperature offsets can cause significant changes 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.

Results

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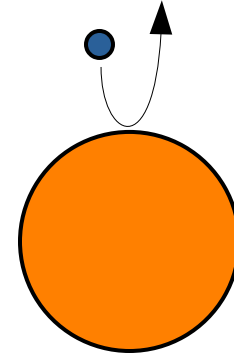
There are multiple processes that can change the temperature of a cluster. Here, we will give a short overview of the two most important ones: collisional and radiative cooling.
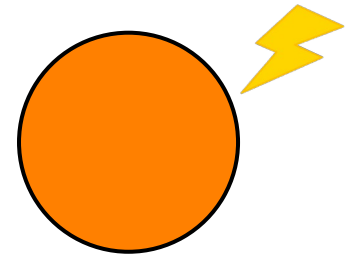
Collisional cooling describes the temperature adjustments of the clusters to the surrounding gas due to elastic collisions with the gas.

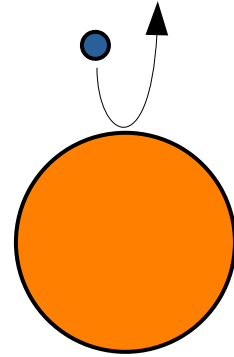Radiative cooling describes the loss of energy via line emission of photons.

- Kinetic – Collisional

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

- Internal – Collisional

$$(\tau_{gc}^{int})^{-1} \approx \frac{2\bar{\alpha}_T}{D_f} n_{gas} r_N^2 \sqrt{\frac{8\pi kT_{gas}}{m_{gas}}}$$

Theory

The thermal adjustment timescales for internal and kinetic cooling are slightly different but show the dependence for the gas phase number density (n_{gas}), the cluster radius (r_N) and the gas phase temperature.

Additional

Evaluating the timescales for a typical exoplanet atmosphere (n_{gas} = 10^{14} cm^{-3}, T_{gas} = 1000 K) and TiO_2 clusters results in timescales of the order of 10^{-6} seconds for both timescales. Since this scales linearly with n_{gas} these timescales become lower for low density environments.

- Kinetic – Collisional

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

- Internal – Collisional

$$(\tau_{gc}^{int})^{-1} \approx \frac{2\bar{\alpha}_T}{D_f} n_{gas} r_N^2 \sqrt{\frac{8\pi kT_{gas}}{m_{gas}}}$$

- Internal – Radiative

Plane and Robertson (2022)
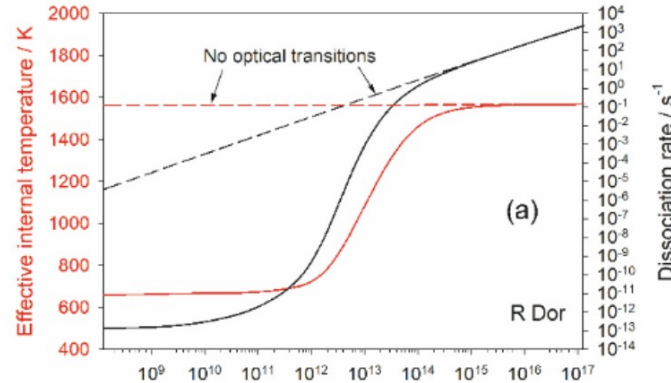
Theory

Radiative cooling is especially efficient via optical lines but can happen via all transitions. The exact calculations are complex and the example for $OSi(OH)_2$ can be found in Plane and Robertson (2022).

Additional

Within a strong radiative field, clusters can also absorb photons via the same lines and experience heating rather than cooling.
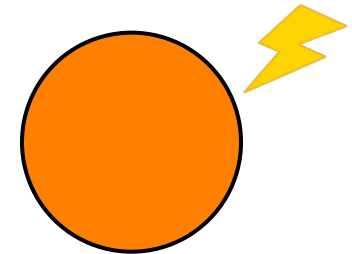
Theory In this section we give an overview over the derivation of the backwards rate. More details can be found in our paper.

Press the arrow to go to the next step!

The law of mass action is derived by minimizing the total Gibbs free energy of the gas. Because changes in internal temperature do not change the pressure or number density of the gas, we can split the Gibbs free energy change due to internal thermal non-equilibrium using ω_i.

$$G^{non-eq}(T_0^{int},...,T_r^{int},T_0^{kin},...,T_r^{kin},p_0,...,p_r,N_0,...,N_r)$$

$$= \sum_{i=0}^{r} G_i^{non-eq}(T_i^{int},T_i^{kin},p_i,N_i)$$

$$= \sum_{i=0}^{r} G_i(T_i^{kin},p_i,N_i) + N_i \, \omega_i(T_i^{kin},T_i^{int}),$$

We use the definition of the chemical potential μ and assume that the number of monomer units is conserved. This conservation is always given in bimolecular association reactions.

$$G^{non-eq}(T_0^{int}, ..., T_r^{int}, T_0^{kin}, ..., T_r^{kin}, p_0, ..., p_r, N_0, ..., N_r)$$

$$= \sum_{i=0}^{r} G_i^{non-eq}(T_i^{int}, T_i^{kin}, p_i, N_i)$$

$$= \sum_{i=0}^{r} G_i(T_i^{kin}, p_i, N_i) + N_i\, \omega_i(T_i^{kin}, T_i^{int}),$$

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

$$G = N\mu$$

Using these three, we can define the Lagrangian function to minimize the Gibbs free energy under conservation of monomer units.

$$G^{non-eq}(T_0^{\text{int}},...,T_r^{\text{int}},T_0^{\text{kin}},...,T_r^{\text{kin}},p_0,...,p_r,N_0,...,N_r)$$

$$= \sum_{i=0}^{r} G_i^{non-eq}(T_i^{\text{int}},T_i^{\text{kin}},p_i,N_i)$$

$$= \sum_{i=0}^{r} G_i(T_i^{\text{kin}},p_i,N_i) + N_i\,\omega_i(T_i^{\text{kin}},T_i^{\text{int}}),$$

$$C = \sum_{i=1}^{r} i\,N_i \qquad G = N\mu$$

$$\mathcal{L} = N_{\text{gas}}\mu_{\text{gas}}(T_{\text{gas}},p) + N_{\text{gas}}kT_{\text{gas}}\ln\left(\frac{N_{\text{gas}}}{N}\right) - \lambda C$$

$$+ \sum_{i=1}^{r} N_i\mu_i(T_i^{\text{kin}},p) + N_i kT_i^{\text{kin}}\ln\left(\frac{N_i}{N}\right)$$

$$+ N_i\,\omega_i(T_i^{\text{kin}},T_i^{\text{int}}) + \lambda i N_i.$$

$$G^{non-eq}(T_0^{int},...,T_r^{int},T_0^{kin},...,T_r^{kin},p_0,...,p_r,N_0,...,N_r)$$

$$= \sum_{i=0}^{r} G_i^{non-eq}(T_i^{int},T_i^{kin},p_i,N_i)$$

$$= \sum_{i=0}^{r} G_i(T_i^{kin},p_i,N_i) + N_i\,\omega_i(T_i^{kin},T_i^{int}),$$

$$C = \sum_{i=1}^{r} i\,N_i \qquad G = N\mu$$

$$\mathcal{L} = N_{gas}\mu_{gas}(T_{gas},p) + N_{gas}kT_{gas}\ln\left(\frac{N_{gas}}{N}\right) - \lambda C$$

$$+ \sum_{i=1}^{r} N_i\mu_i(T_i^{kin},p) + N_ikT_i^{kin}\ln\left(\frac{N_i}{N}\right)$$

$$+ N_i\,\omega_i(T_i^{kin},T_i^{int}) + \lambda i N_i.$$

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

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

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$$G^{non-eq}(T_0^{int},...,T_r^{int},T_0^{kin},...,T_r^{kin},p_0,...,p_r,N_0,...,N_r)$$

$$= \sum_{i=0}^{r} G_i^{non-eq}(T_i^{int},T_i^{kin},p_i,N_i)$$

$$= \sum_{i=0}^{r} G_i(T_i^{kin},p_i,N_i) + N_i\,\omega_i(T_i^{kin},T_i^{int}),$$

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$$+ \sum_{i=1}^{r} N_i\mu_i(T_i^{kin},p) + N_ikT_i^{kin}\ln\left(\frac{N_i}{N}\right)$$

$$+ N_i\,\omega_i(T_i^{kin},T_i^{int}) + \lambda i N_i.$$

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

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

$$\frac{\partial\mathcal{L}}{\partial N_j} = \mu_j(T_j^{kin},p) + kT_j^{kin}\ln\left(\frac{N_j}{N}\right) + \omega_j(T_j^{kin},T_j^{int})$$

$$+ \lambda j x_1 + kT_j^{kin}\frac{N-N_j}{N} - \sum_{\substack{i=0 \\ i\neq j}}^{r}\frac{N_ikT_i^{kin}}{N},$$

$$\approx \mu_j(T_j^{kin},p) + kT_j^{kin}\ln\left(\frac{N_j}{N}\right) + \omega_j(T_j^{kin},T_j^{int})$$

$$+ \lambda j + k(T_j^{kin} - T_{gas}),$$

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$$G^{non-eq}(T_0^{int},...,T_r^{int},T_0^{kin},...,T_r^{kin},p_0,...,p_r,N_0,...,N_r)$$

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$$= \sum_{i=0}^{r} G_i(T_i^{kin},p_i,N_i) + N_i\,\omega_i(T_i^{kin},T_i^{int}),$$

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

$$G = N\mu$$

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

$$\mathcal{L} = N_{gas}\mu_{gas}(T_{gas},p) + N_{gas}kT_{gas}\ln\left(\frac{N_{gas}}{N}\right) - \lambda C$$

$$+ \sum_{i=1}^{r} N_i\mu_i(T_i^{kin},p) + N_i kT_i^{kin}\ln\left(\frac{N_i}{N}\right)$$

$$+ N_i\,\omega_i(T_i^{kin},T_i^{int}) + \lambda i N_i.$$

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

$$N_{gas}T_{gas} \gg \sum_{i=1}^{r} N_i T_i^{kin}$$

$$\frac{\partial \mathcal{L}}{\partial N_j} = \mu_j(T_j^{kin},p) + kT_j^{kin}\ln\left(\frac{N_j}{N}\right) + \omega_j(T_j^{kin},T_j^{int})$$

$$+ \lambda j x_1 + kT_j^{kin}\frac{N-N_j}{N} - \sum_{\substack{i=0 \\ i\neq j}}^{r}\frac{N_i kT_i^{kin}}{N},$$

$$\approx \mu_j(T_j^{kin},p) + kT_j^{kin}\ln\left(\frac{N_j}{N}\right) + \omega_j(T_j^{kin},T_j^{int})$$

$$+ \lambda j + k(T_j^{kin} - T_{gas}),$$

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$$G^{non-eq}(T_0^{int},...,T_r^{int},T_0^{kin},...,T_r^{kin},p_0,...,p_r,N_0,...,N_r)$$

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$$C = \sum_{i=1}^{r} i\,N_i \qquad G = N\mu$$

$$\mathcal{L} = N_{gas}\mu_{gas}(T_{gas},p) + N_{gas}kT_{gas}\ln\left(\frac{N_{gas}}{N}\right) - \lambda C$$

$$+ \sum_{i=1}^{r} N_i\mu_i(T_i^{kin},p) + N_i kT_i^{kin}\ln\left(\frac{N_i}{N}\right)$$

$$+ N_i\,\omega_i(T_i^{kin},T_i^{int}) + \lambda i N_i.$$

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

$$N_{gas}T_{gas} \gg \sum_{i=1}^{r} N_i T_i^{kin}$$

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

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

$$\frac{\partial\mathcal{L}}{\partial N_j} = \mu_j(T_j^{kin},p) + kT_j^{kin}\ln\left(\frac{N_j}{N}\right) + \omega_j(T_j^{kin},T_j^{int})$$

$$+ \lambda j x_1 + kT_j^{kin}\frac{N-N_j}{N} - \sum_{\substack{i=0\\i\neq j}}^{r}\frac{N_i kT_i^{kin}}{N},$$

$$\approx \mu_j(T_j^{kin},p) + kT_j^{kin}\ln\left(\frac{N_j}{N}\right) + \omega_j(T_j^{kin},T_j^{int})$$

$$+ \lambda j + k(T_j^{kin}-T_{gas}),$$

Mathematical derivation

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

$$C = \sum_{i=1}^{r} i\,N_i \qquad G = N\mu$$

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

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

$$N_{gas}T_{gas} \gg \sum_{i=1}^{r} N_i T_i^{kin}$$

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

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

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

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

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

Go to the results!

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