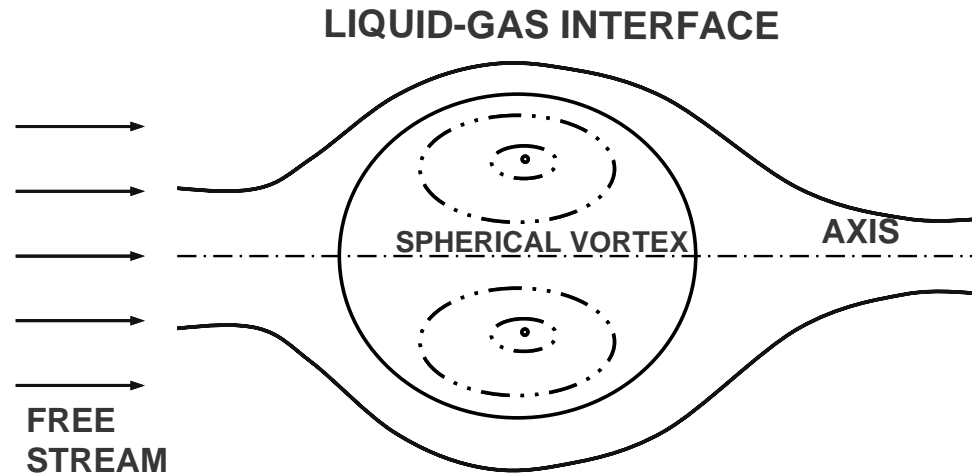


Aerosol water droplet evaporation modelling

S. Tonini and G.E. Cossali



Introduction



Evaporation rate and energy equation

$$\frac{dm_d}{dt} = -\dot{m}_{ev}$$

$$\frac{d(m_d c_{vl} T_d)}{dt} + \dot{m}_{ev} h_{lv} = \pi D_d Nu_c k_f (T_\infty - T_d)$$



Evaporation rate modelling

Only diffusion: *Maxwell model*

$$\dot{m}_{ev} = 4\pi R_d D_v (\rho_{v,s} - \rho_{v,\infty}) = 4\pi R_d D_v \rho (\chi_{v,s} - \chi_{v,\infty})$$

Diffusion and convection (Stefan Flow), $\rho = \text{const}$

$$\dot{m}_{ev} = 4\pi R_d D_v \ln \frac{\rho - \rho_{v,\infty}}{\rho - \rho_{v,s}} = 4\pi R_d D_v \rho \ln \frac{1 - \chi_{v,\infty}}{1 - \chi_{v,s}}$$



Evaporation rate modelling

Diffusion and convection (Stefan Flow), $\rho = \text{const}$

$$\begin{cases} \nabla (\rho_v(r) U(r)) = \nabla (D_{vg} \rho \nabla \chi_v(r)) \\ \nabla (\rho_g(r) U(r)) = \nabla (D_{gv} \rho \nabla \chi_g(r)) \end{cases}$$

$$\begin{cases} \rho = \rho_v(r) + \rho_g(r) = \text{const} \\ U(r) = \frac{\dot{m}_{ev}}{4\pi r^2 \rho} \\ D_{vg} = D_{gv} = D_v; \quad u_l = 0; \quad u_i \simeq 0 \end{cases}$$



Evaporation rate modelling

Diffusion and convection (Stefan Flow), $\rho = \text{const}$

$$\left\{ \begin{array}{l} \ln \frac{\rho_{g,\infty}}{\rho_{g,s}} = \ln \frac{\chi_{g,\infty}}{\chi_{g,s}} = \frac{\dot{m}_{ev}}{4\pi D_v \rho R_d} \\ \chi_{v,s} = 1 - \chi_{g,s} = 1 - \frac{1}{\chi_{g,\infty}} \exp\left(\frac{\dot{m}_{ev}}{4\pi D_v \rho R_d}\right) \end{array} \right.$$

The estimation of the mass fraction of the vaporising species closed to the surface, $\chi_{v,s} = \rho_{v,s} / \rho$, depends on the equilibrium assumption imposed at the liquid/gas interface.



Interface equilibrium assumption

Equilibrium (Hydro-dynamic) model: Clausius-Clapeyron equation

$$\chi_{v,s}^{eq} = \frac{\zeta_{v,s}^{eq}}{\zeta_{v,s}^{eq} (1-\theta) + \theta}$$
$$\zeta_{v,s}^{eq} = \frac{P_s}{P_\infty} = \frac{P_{atm}}{P_\infty} \exp \left[\frac{h_{lv}}{R/Mw_v} \left(\frac{1}{T_{boil}} - \frac{1}{T_d} \right) \right]$$

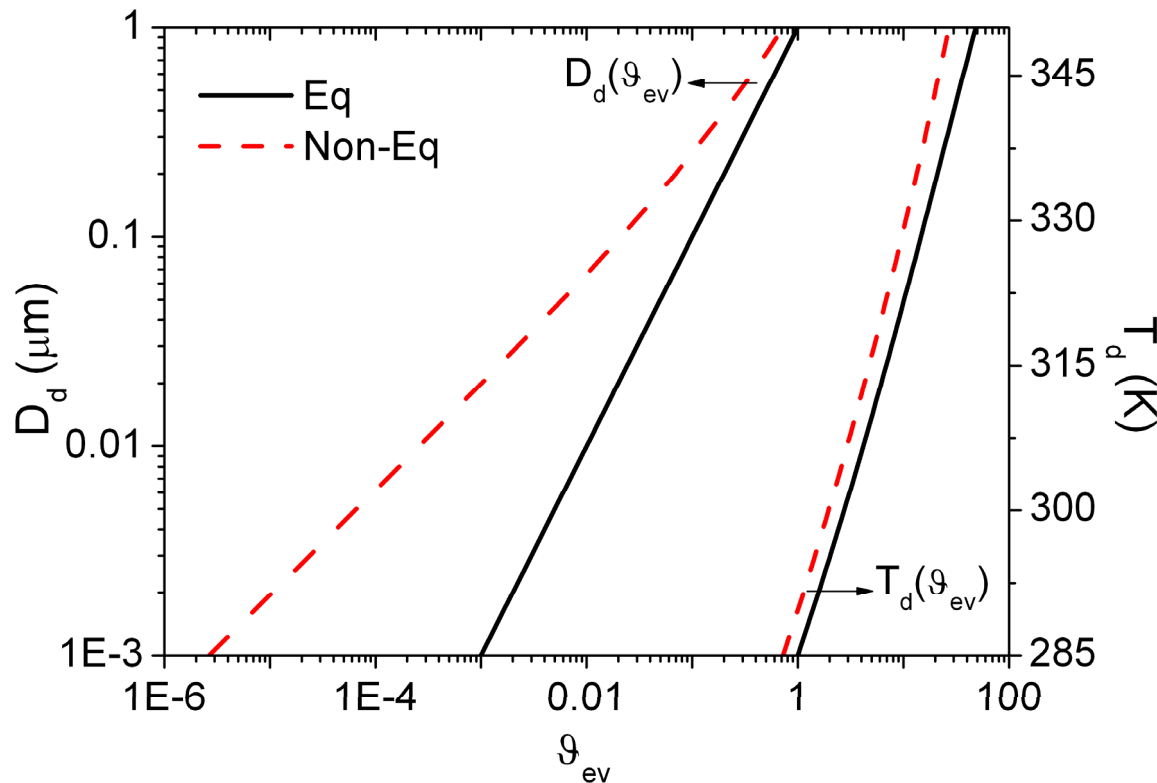
NON-Equilibrium (Kinetic theory) model: Hertz-Knudsen equation

$$\zeta_{v,s}^{non-eq} = \frac{P_v}{P_\infty} = \frac{P_s}{P_\infty} - \frac{\dot{m}_{ev}}{P_\infty \alpha_\varepsilon \pi D_d^2 \sqrt{\frac{Mw_v}{2\pi RT_d}}}$$



Sub-micrometer droplet vaporisation

Equilibrium versus non-equilibrium model



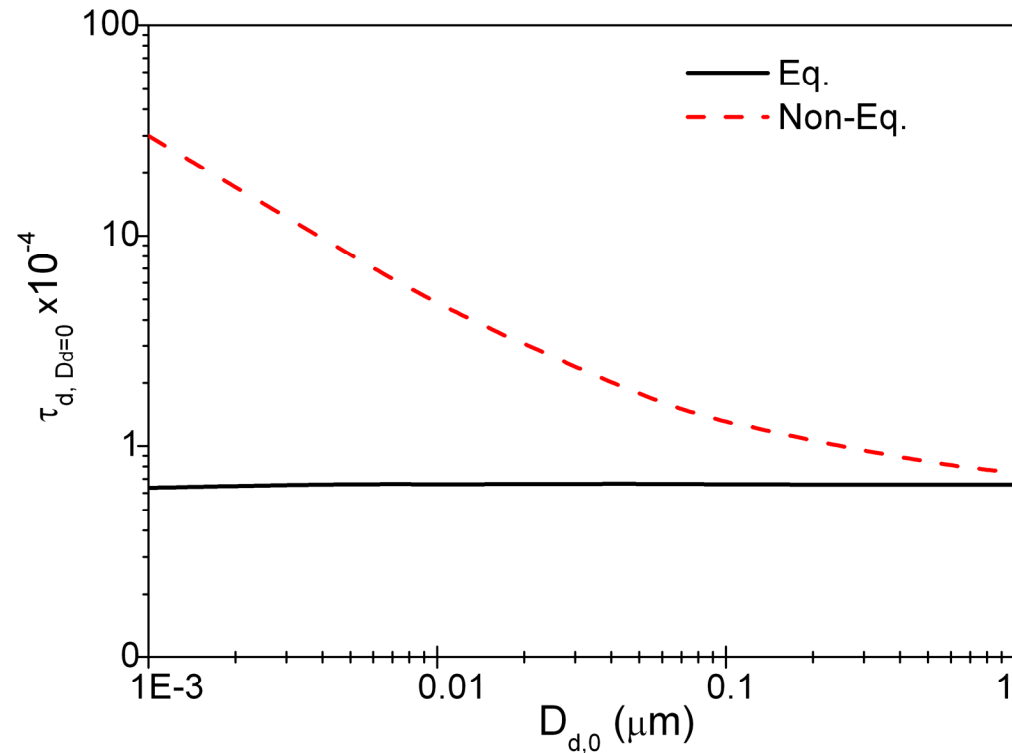
Non-equilibrium assumption leads to a **remarkable decrease** of the evaporation rate, compared to the equilibrium one.

$$g_{ev} = \frac{\dot{m}_{ev}(D_d, T_d)}{\dot{m}_{ev}(D_d = 1\mu\text{m}, T_d = 285\text{K})}$$



Sub-micrometer droplet vaporisation

Equilibrium versus non-equilibrium model



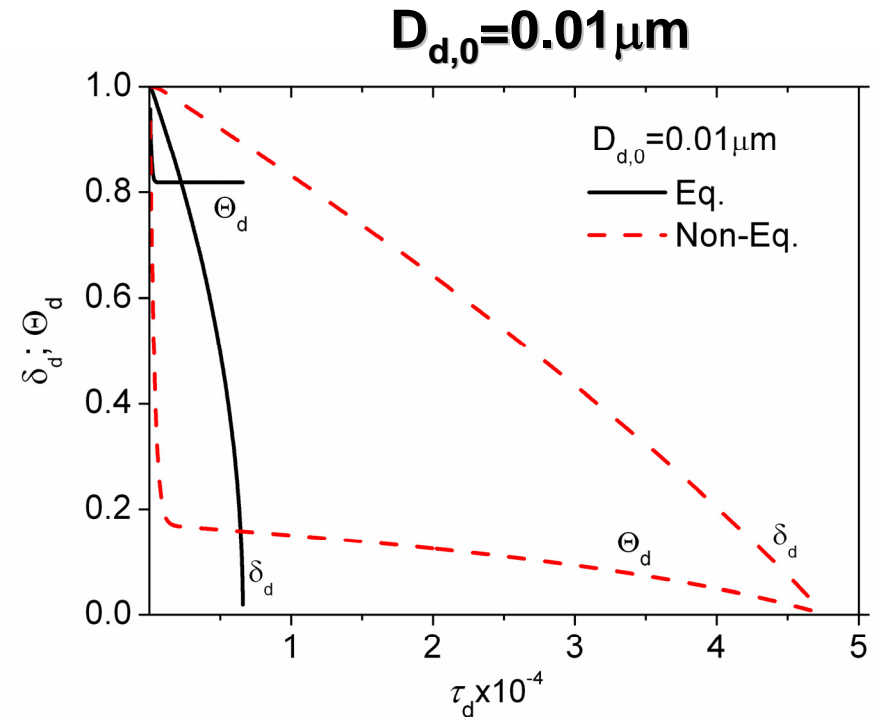
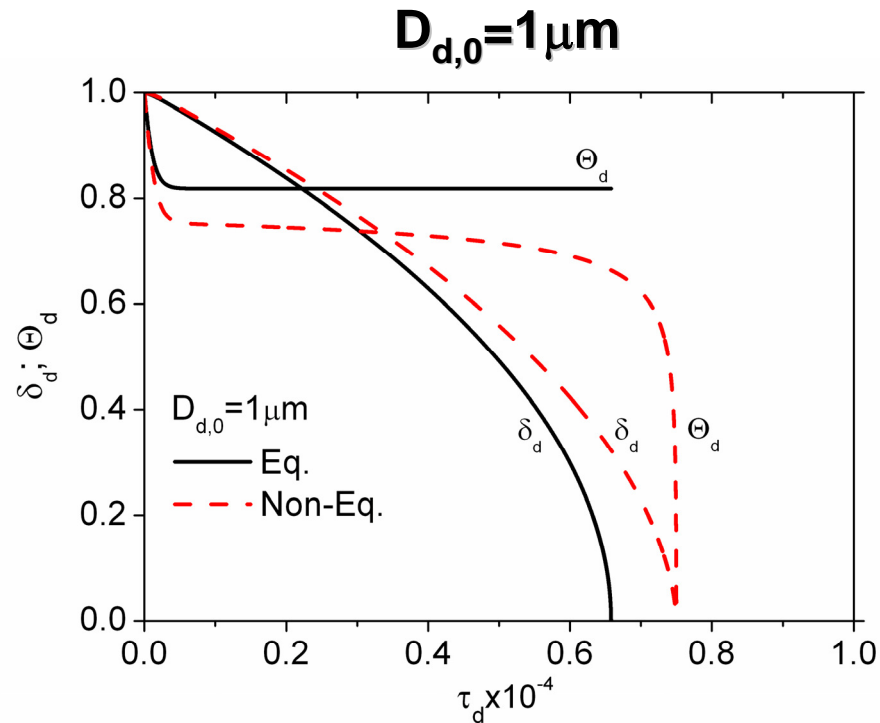
Non-equilibrium model predicts considerable **longer** droplet **lifetime**.

$$\tau_d = t D_{vg} / D_{d,0}^2$$



Sub-micrometer droplet vaporisation

Equilibrium versus non-equilibrium model



Non-equilibrium model does not predict **liquid bulk temperature**.
The droplet lifetime is remarkably increased.



$$\delta_d = D_d / D_{d,0}; \quad \Theta_d = (T_d - T_\infty) / (T_{d,0} - T_\infty); \quad \tau_d = t D_{vg} / D_{d,0}^2$$

Sub-micrometer droplet vaporisation

Equilibrium model investigation: main conclusions

The droplet temperature predicted by the non-equilibrium model does not reach **steady state bulk temperature**, since the instantaneous temperature value is function of the droplet size

$$\frac{D_d^2}{6} c_{v_l} \frac{dT_d}{dt} + D_{vg} \rho_f Sh \ln(1 + B_\chi) (h_{lv} - c_{v_l} T_d) = Nu_c k_f (T_\infty - T_d)$$

$$\chi_{v,s} = \begin{cases} \chi_{v,s}^{eq}(T_d): \text{equilibrium model} \\ \chi_{v,s}^{non-eq}(T_d, D_d): \text{non-equilibrium model} \end{cases}$$



Effect of surface curvature

The saturation vapour pressure, in a presence of a curved interface between the liquid and vapour, is corrected by the *Kelvin equation*, which takes into account the effect of **liquid surface tension**:

$$P_{d,s}^* = P_s \exp \frac{4\sigma_l M w_v}{\rho_l D_d R T_d}$$

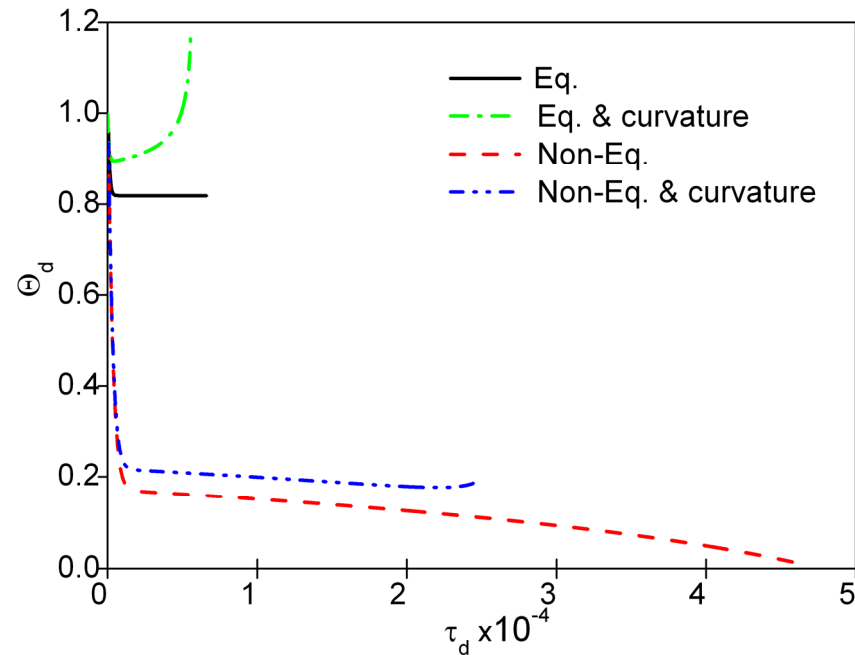
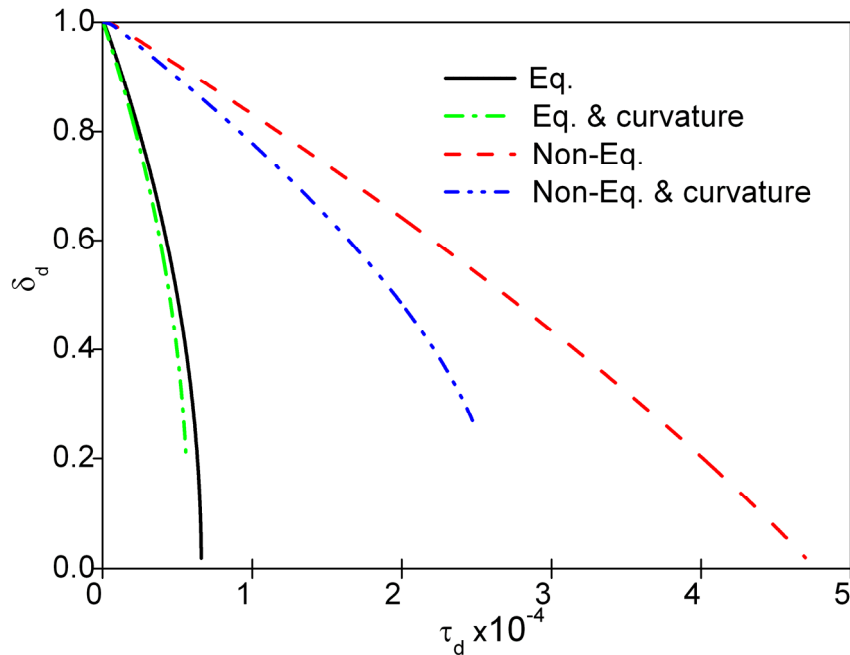
The **effect of liquid surface tension** on evaporation rate **may be cancelled** by the opposite contribution from **non-equilibrium** assumption.



Sub-micrometer droplet vaporisation

Effect of equilibrium model and surface curvature

$D_{d,0} = 0.01 \mu\text{m}$



$$\delta_d = D_d / D_{d,0}; \quad \Theta_d = (T_d - T_\infty) / (T_{d,0} - T_\infty); \quad \tau_d = t D_{vg} / D_{d,0}^2$$



Effect of surface curvature

The **effect of curvature** induces the model to predict '**critical**' values for the liquid temperature when the droplet diameter is smaller than a **characteristic length** that is function of liquid thermal properties.

Characteristic length of droplet size

$$l_{P_{d,s}}^* = \frac{4\sigma_l M w_v}{\rho_l R T_d}$$

Corrected boiling temperature

$$T_{d,b}^* = T_b \left(1 - \frac{4\sigma_l}{\rho_l D_d h_{lv}} \right)$$

T_d	$l_{P_{d,s}}^* (T_d)$	$T_{d,b}^* (l_{P_{d,s}}^*)$
(K)	(nm)	(K)
274	2.3	354
285	2.2	353
300	2.1	352
330	1.9	349
350	1.8	347



Effect of surface curvature

Main conclusions

- The increase of the droplet vaporisation rate, as predicted by the model assuming equilibrium conditions and including the effect of surface curvature, leads to the reduction of **liquid temperature** as vaporisation takes place, down to '**critical**' values.
- **Kelvin equation** predicts **faster vaporisation** compared to the case neglecting the effect of curvature, reducing the **opposite effect** of lower evaporation rate as predicted by the **non-equilibrium assumption**.



Evaporation rate close to boiling conditions

Only diffusion: ($U = 0$)

$$\overset{\sim}{\dot{m}}_{ev}^{eq} = \frac{\dot{m}}{4\pi R_d D_v \rho} = \chi_{v,s} - \chi_{v,\infty} = \chi_{g,\infty} - \chi_{g,s}$$

$$\overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \chi_{g,\infty} - \frac{\overset{\chi_{g,s}}{P_T - P_{v,s}}}{\frac{R}{Mw_g} T_{d,s} \rho} + \frac{\dot{m}}{4\pi R_d D_v \rho} \sqrt{\frac{2\pi Mw_g^2 D_v^2}{RT_{d,s} Mw_v R_d^2}} \overset{\Psi}{}$$

$$\overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \chi_{g,\infty} - \Pi + \tilde{\dot{m}} \Psi = \frac{\chi_{g,\infty} - \chi_{g,s}}{1 + \Psi}$$



Evaporation rate close to boiling conditions

Diffusion and convection: ($U \neq 0$)

$$\overset{\sim}{\dot{m}}_{ev}^{eq} = \ln \frac{\rho_{g,\infty}}{\rho_{g,s}} = \ln \frac{\frac{\rho_{g,\infty}}{\rho}}{\frac{P_T - P_{v,s}}{\frac{R}{Mw_g} T_{d,s} \rho}} = \ln \frac{\chi_{g,\infty}}{\chi_{g,s}}$$

$$\overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \ln \frac{\frac{\rho_{g,\infty}}{\rho}}{\frac{P_T - P_{v,s}}{\frac{R}{Mw_g} T_{d,s} \rho} + \frac{\dot{m}}{4\pi R_d D_v \rho} \sqrt{\frac{2\pi Mw_g^2 D_v^2}{RT_{d,s} Mw_v R_d^2}}} = \ln \frac{\chi_{g,\infty}}{\chi_{g,s} + \overset{\sim}{\dot{m}} \Psi}$$

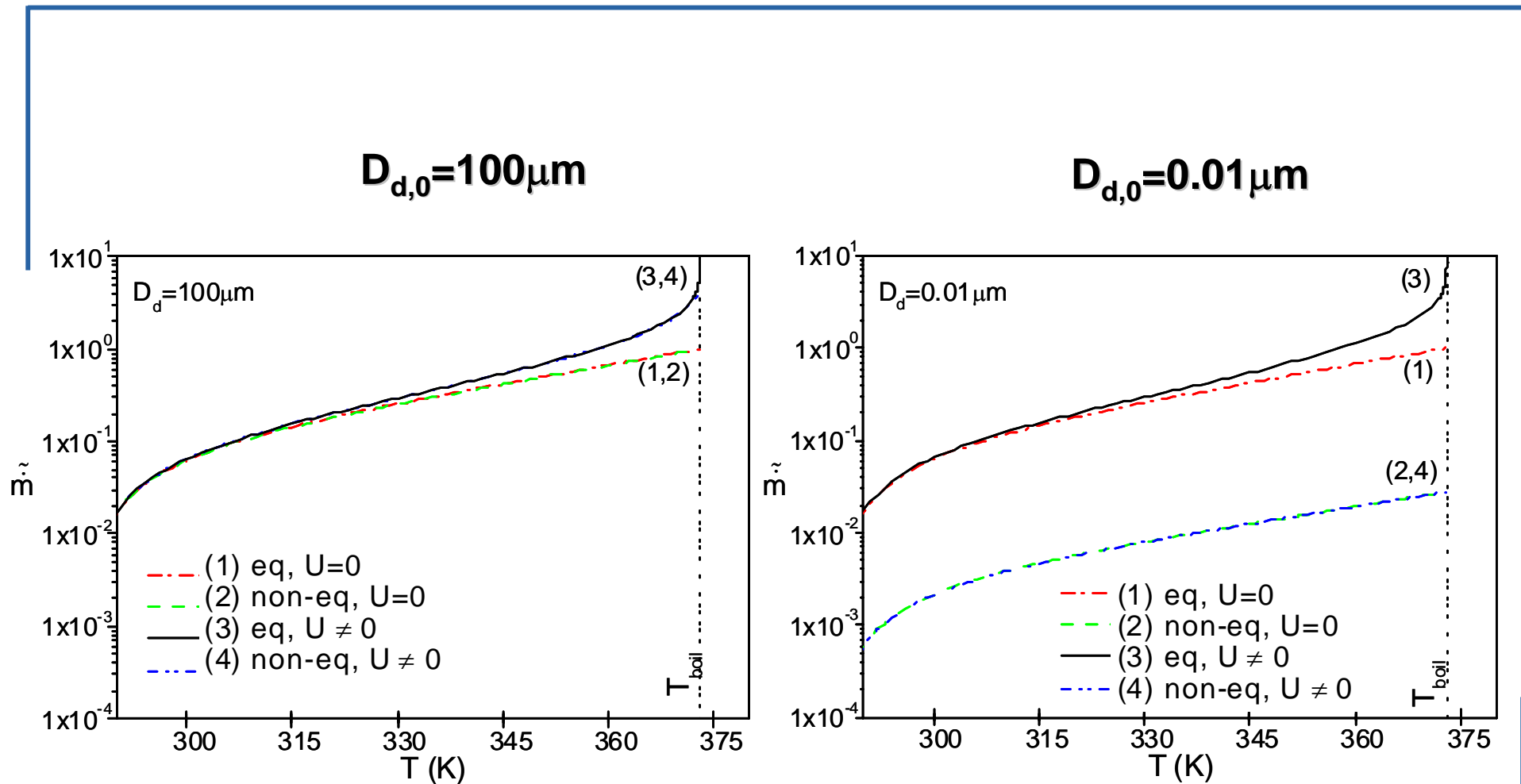


Evaporation rate close to boiling conditions

	Diffusion ($U = 0$)	Diffusion+Convection ($U \neq 0$)
Equilibrium	$\overset{\sim}{\dot{m}}_{ev}^{eq} = \chi_{g,\infty} - \chi_{g,s}$	$\overset{\sim}{\dot{m}}_{ev}^{eq} = \ln \frac{\chi_{g,\infty}}{\chi_{g,s}}$
NON-equilibrium	$\overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \frac{\chi_{g,\infty} - \chi_{g,s}}{1 + \Psi}$	$\overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \ln \frac{\chi_{g,\infty}}{\chi_{g,s} + \overset{\sim}{\dot{m}} \Psi}$



Evaporation rate close to boiling conditions



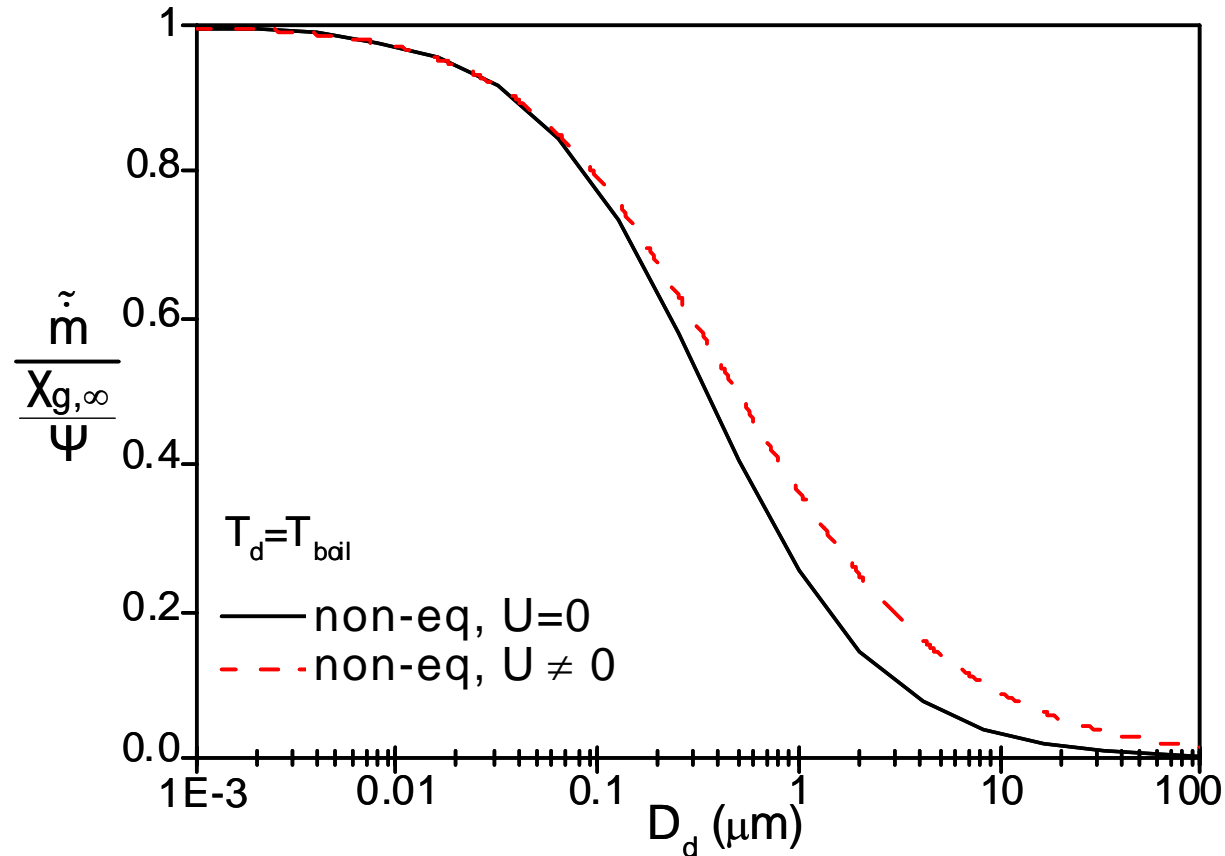
Evaporation rate close to boiling conditions

$$\begin{cases} T_d = T_{boil} \\ P_s = P_T \\ \chi_{g,s} = 0 \end{cases}$$

Diffusion $(U = 0)$	Diffusion+Convection $(U \neq 0)$
$\overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \frac{\chi_{g,\infty}}{1 + \Psi}$ $\lim_{R_d \rightarrow 0} \overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \frac{\chi_{g,\infty}}{\Psi}$	$\overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \ln \frac{\chi_{g,\infty}}{\overset{\sim}{\dot{m}} \Psi}$ $\lim_{R_d \rightarrow 0} \overset{\sim}{\dot{m}}_{ev}^{NON-eq} = \frac{\chi_{g,\infty}}{\Psi}$



Evaporation rate close to boiling conditions



The effect of **Stefan flow**, predicted by the non-equilibrium model, **reduces** with droplet size becoming **smaller than $0.1 \mu\text{m}$**



Conclusions and further step

- **Non-equilibrium** model plays a role on the evaporation rate with droplet size less than **few micrometers** (aerosol range dimension). It predicts **slower** vaporisation.
- Non-equilibrium and **surface curvature** correction predict vaporisation close to **boiling conditions** at the end of lifetime.
- **Equilibrium** model taking into account the Stefan flow effect **diverge** at boiling conditions, while **non-equilibrium** model **does not**.
- **Stefan flow**, predicted by the non-equilibrium model, **reduces** with droplet size less than **0.1 μm**
- *Derivation of a general equation for the evaporation rate: relaxation of assumption of $\rho = \text{const}$.*



References

S. Tonini, *Heat and mass transfer modelling of sub-micrometer droplets under atmospheric pressure conditions*, accepted for publication on *Atomization and Sprays*, 2009.

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Thank you for your attention

