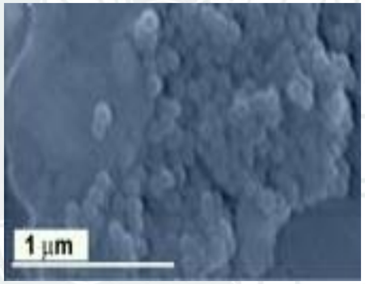
Keimbildung

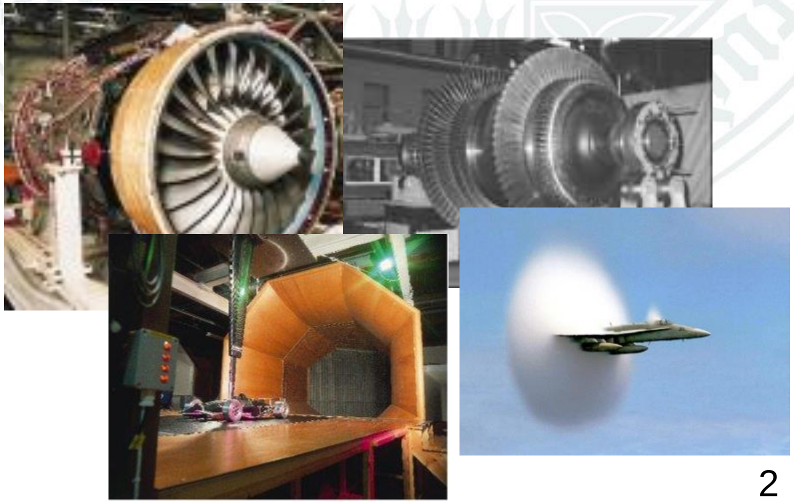
Department für Chemie
Physikalische Chemie
Universität zu Köln

Dr. Judith Wölk

Motivation



- **Atmosphärische Aerosol Bildung**
- **Partikel Herstellung:**
  - Bildung von Nanokristallen
  - Herstellung von qualitativ hochwertigen Pudern
  - Medizin: Bildung von Gallensteinen



- **Kontrolle der Keimbildung in**
  - Turbinen, Dampfturbinen
  - Reaktionsgefäßen
  - Windtunneln
  - Düsenflugzeugen

Motivation

Grundlagen

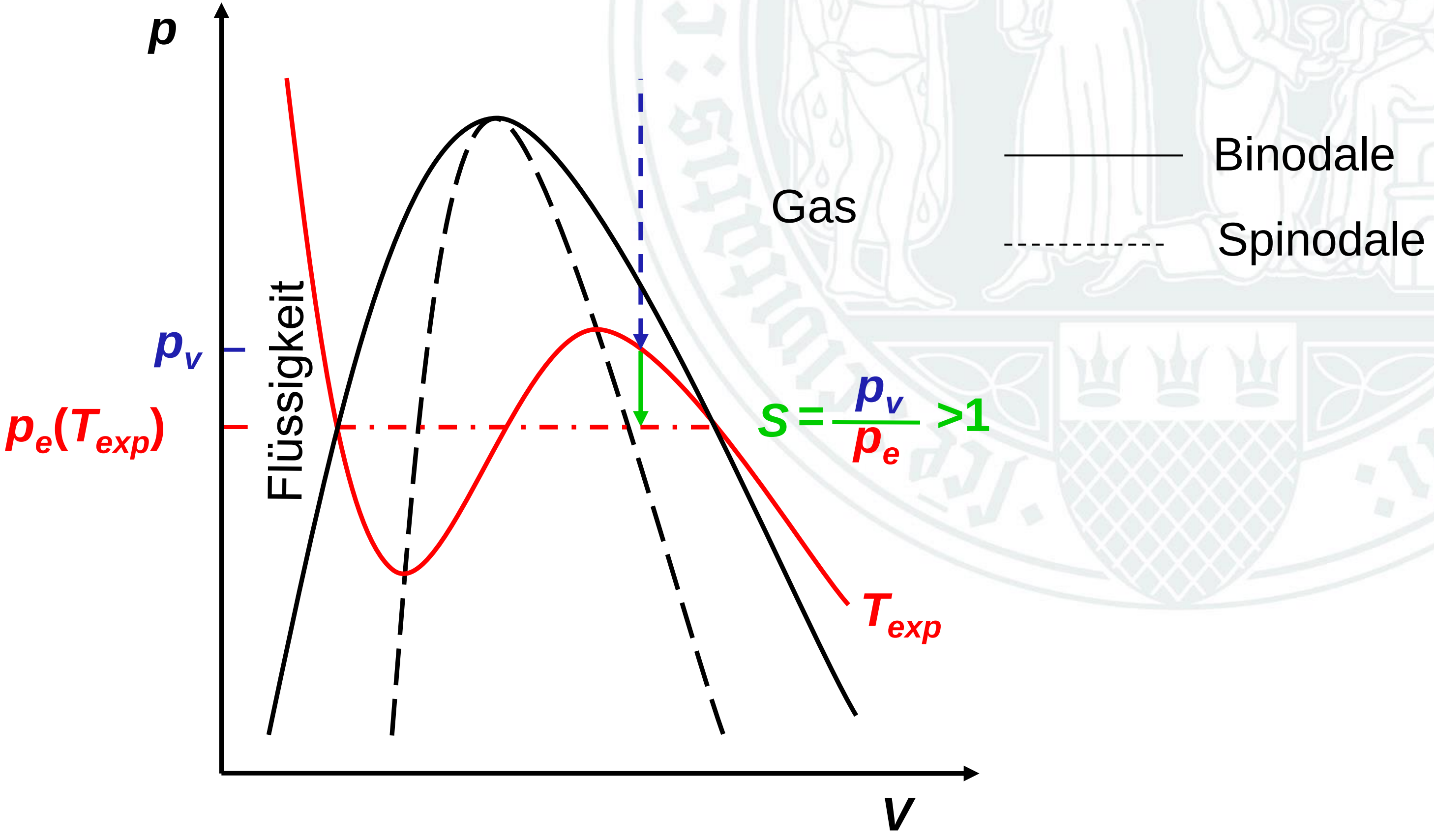
- **Keim:**

  Kleiner Körper, einer neuen Phase, der sich mit der ihn umgebenden Mutterphase im labilen Gleichgewicht befindet.

Grundlagen

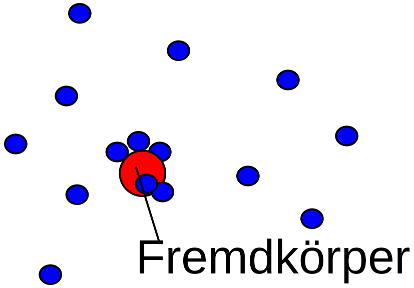
Keimbildung: Phasenübergang erster Ordnung

gasförmig → flüssig



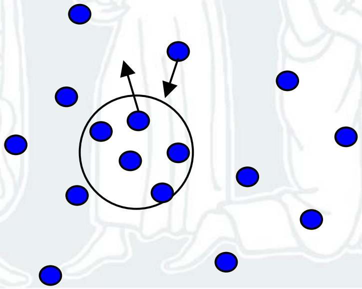
Grundlagen

Heterogene Keimbildung



Keime, die durch Anlagerung der sich ausscheidenden Substanz an einem Fremdkörper entstehen

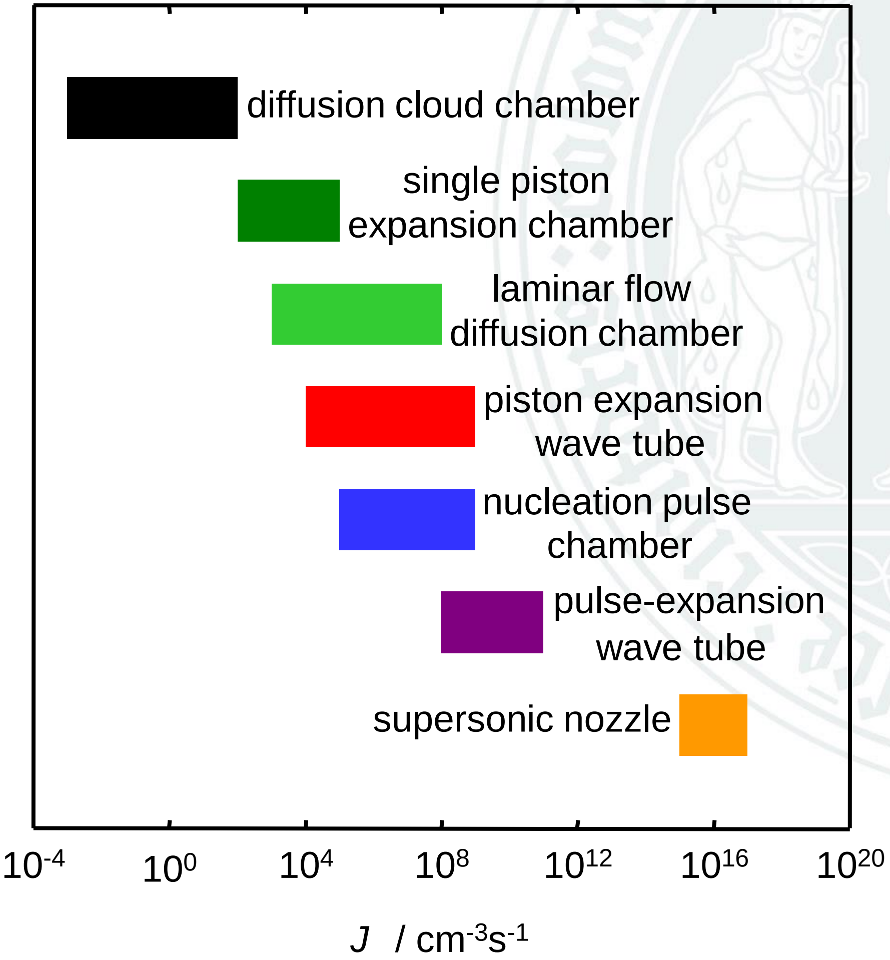
Homogene Keimbildung



Keime, die durch eine vielstufige homogene Reaktion entstehen.

- Wasser
- Alkohole
- Argon
-

Experimentelle Methoden

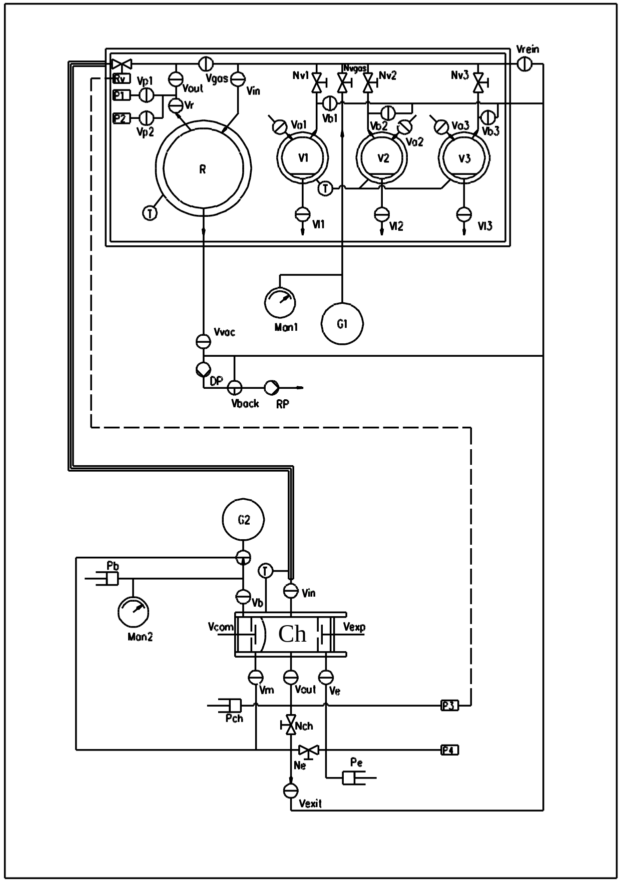


Helsinki

Columbus, Ohio

Keimbildungsrate: Zahl der Teilchen die pro cm^{-3} und Sekunde gebildet werden

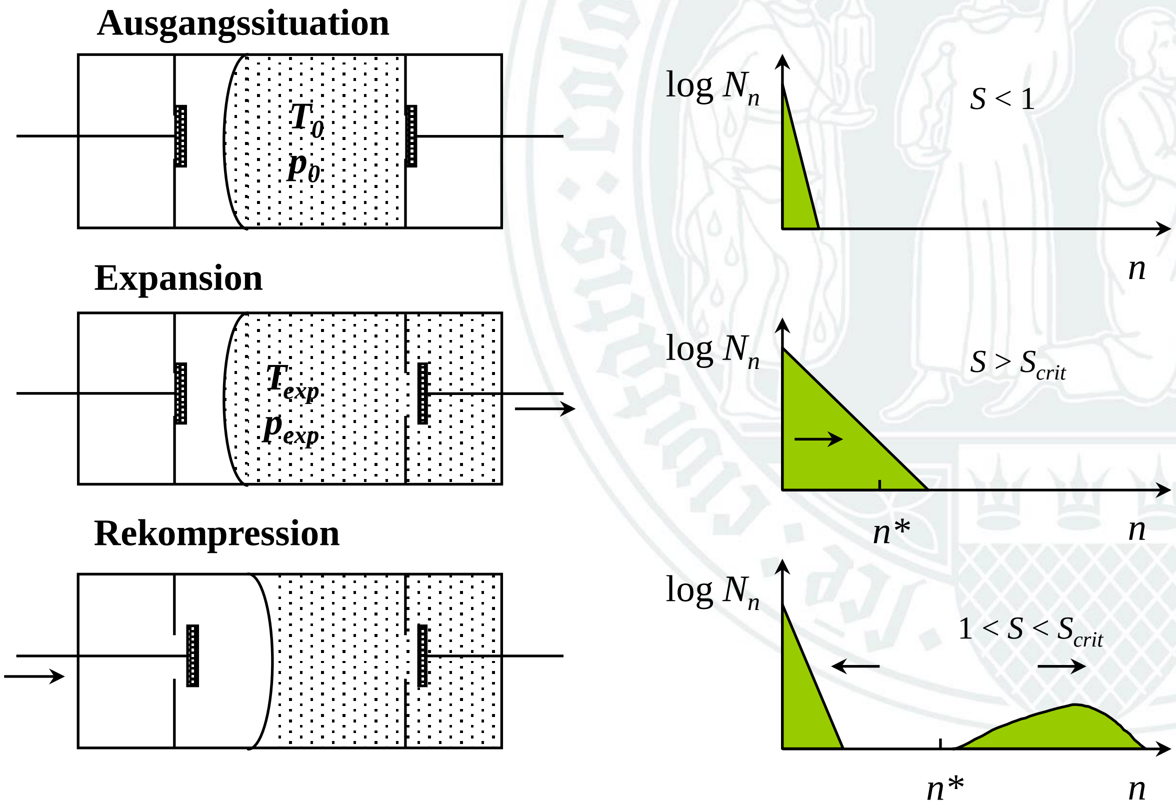
Nukleationspulskammer



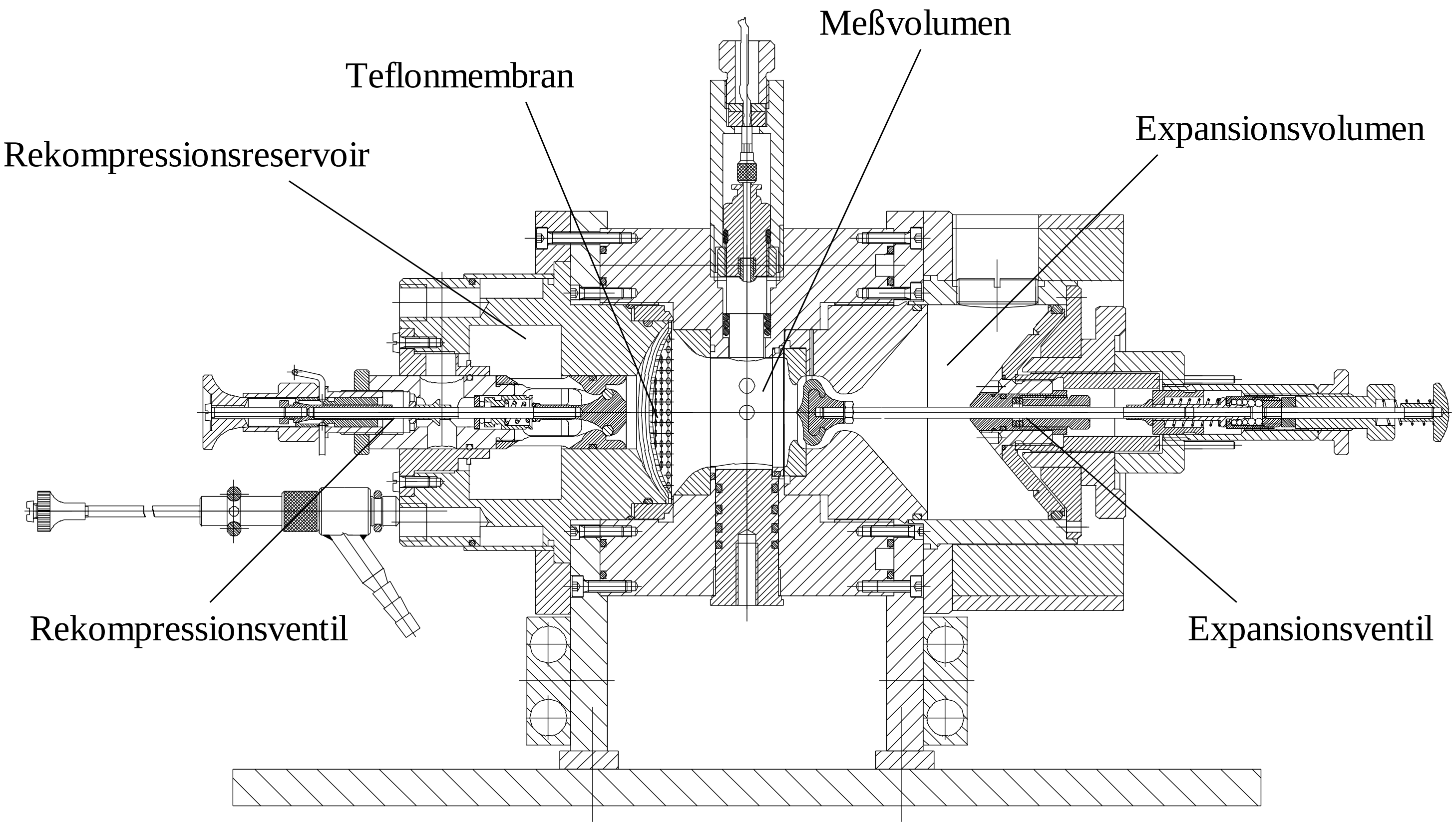
Schematische Darstellung der Messapparatur

V1, V2, V3	Verdampfer
P1, P2, P3, P4	MKS Baratrons
R	Mischkolben
N_{Vi}	Nadelventile
V_i	Absperrventile
P_i	Regelvolumina
G1	Argongasflasche
G2	Stickstoffgasflasche
T	Thermostaten
R_v	elektronisches Regelventil
Man1, Man2	analoge Manometer
Ch	Nukleationspulskammer
-----	elektronische Regelleitung

Nukleationspulskammer

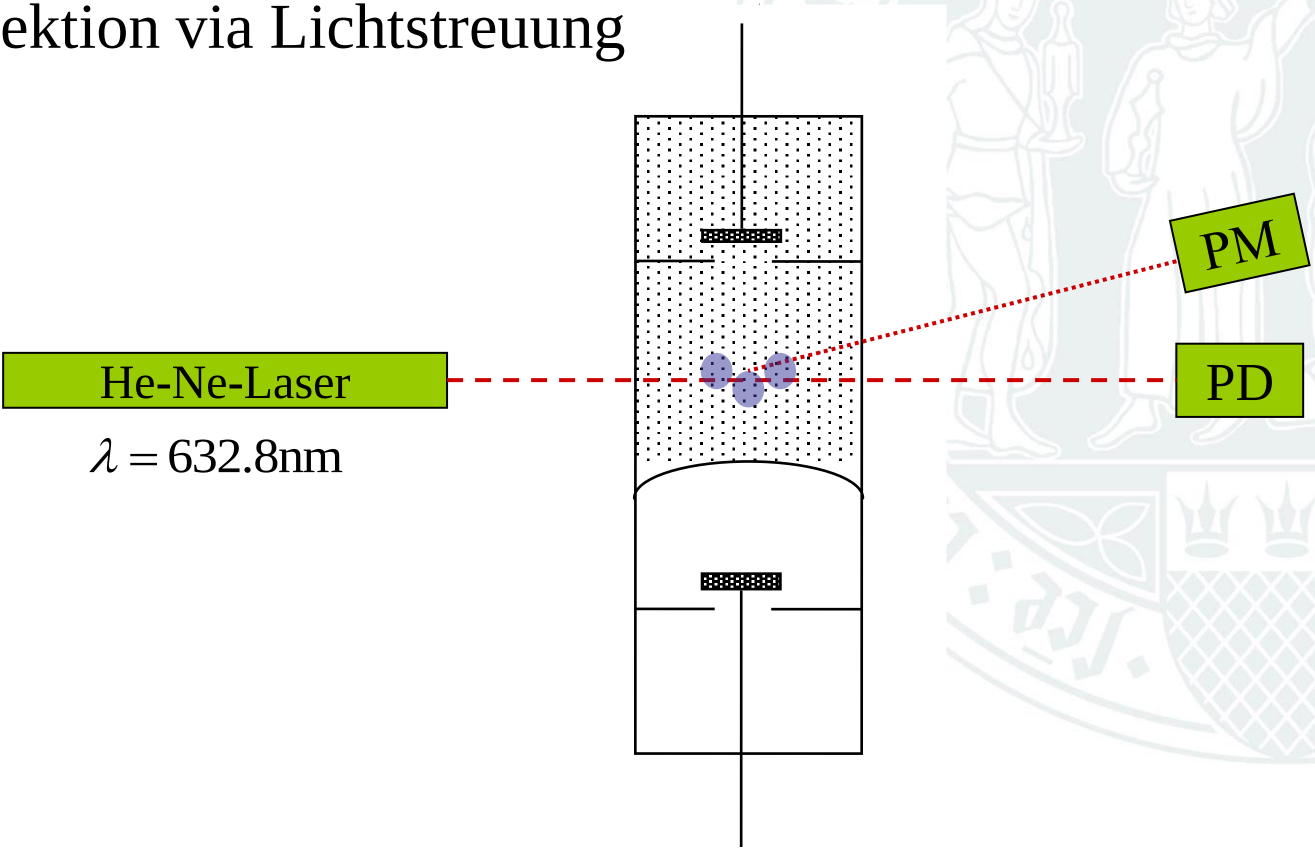


Nukleationspulskammer



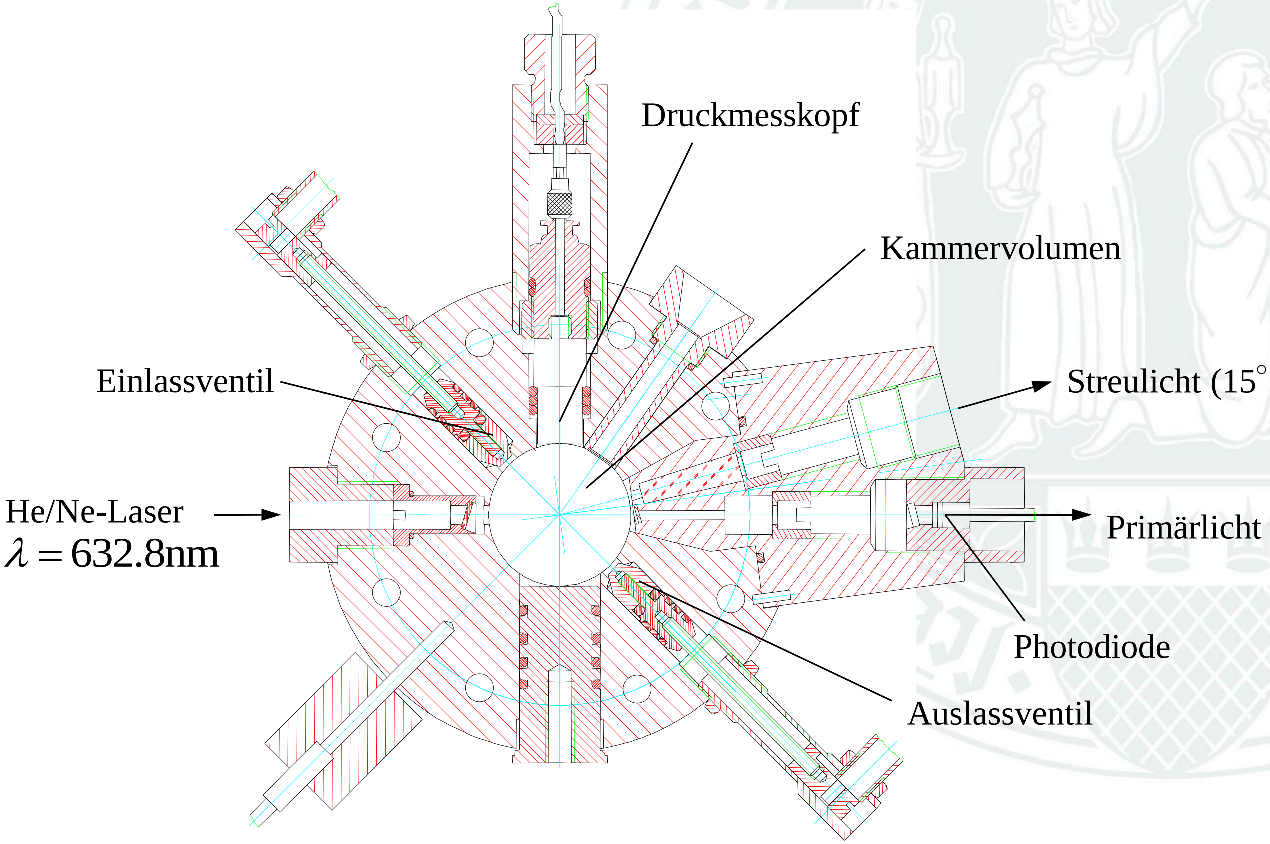
Nukleationspulskammer

Detektion via Lichtstreuung



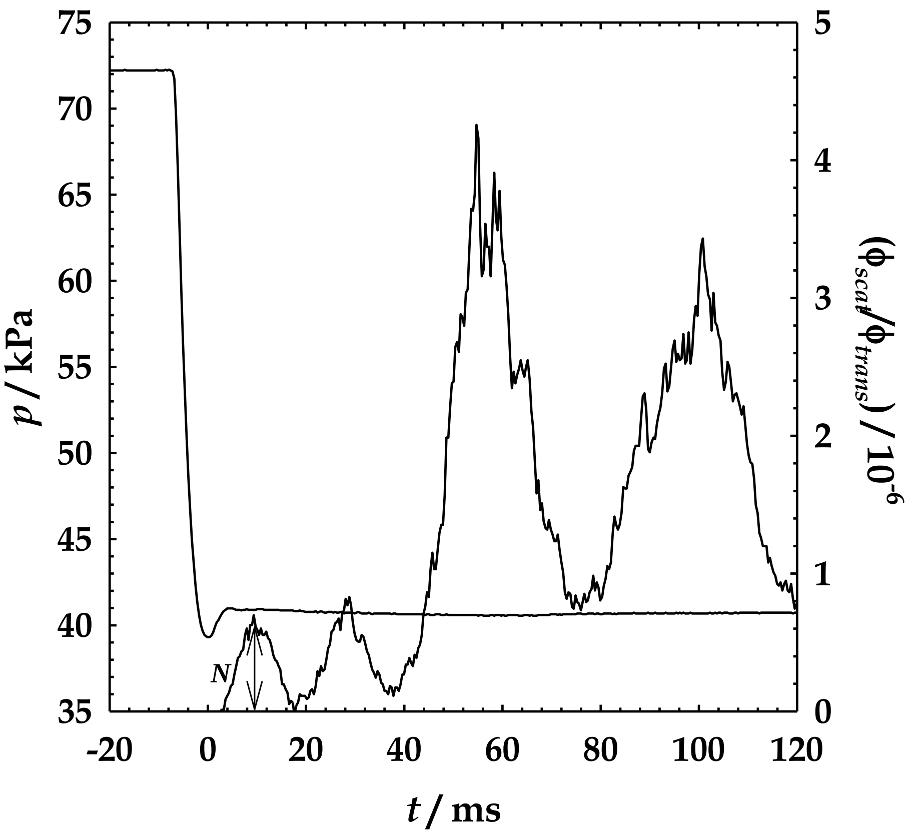
Mie-Streuung: Streuung an sphärischen Objekten,
deren Durchmesser in etwa der Wellenlänge der Strahlung entspricht.

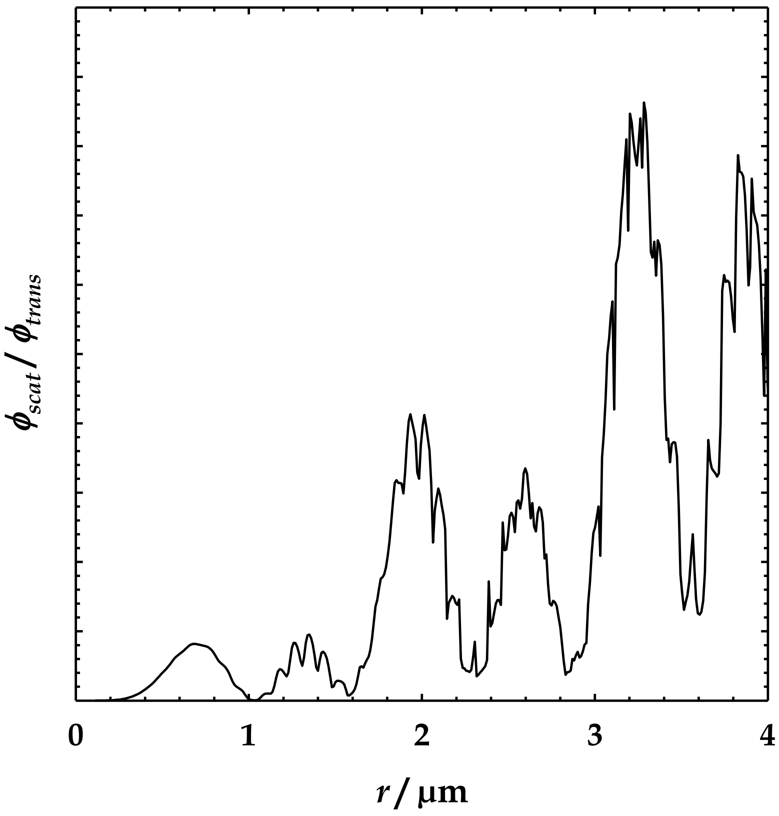
Nukleationpulskammer



CAMS: P. E. Wagner, J. Colloid Interface Sci. 105, 456 (1985)

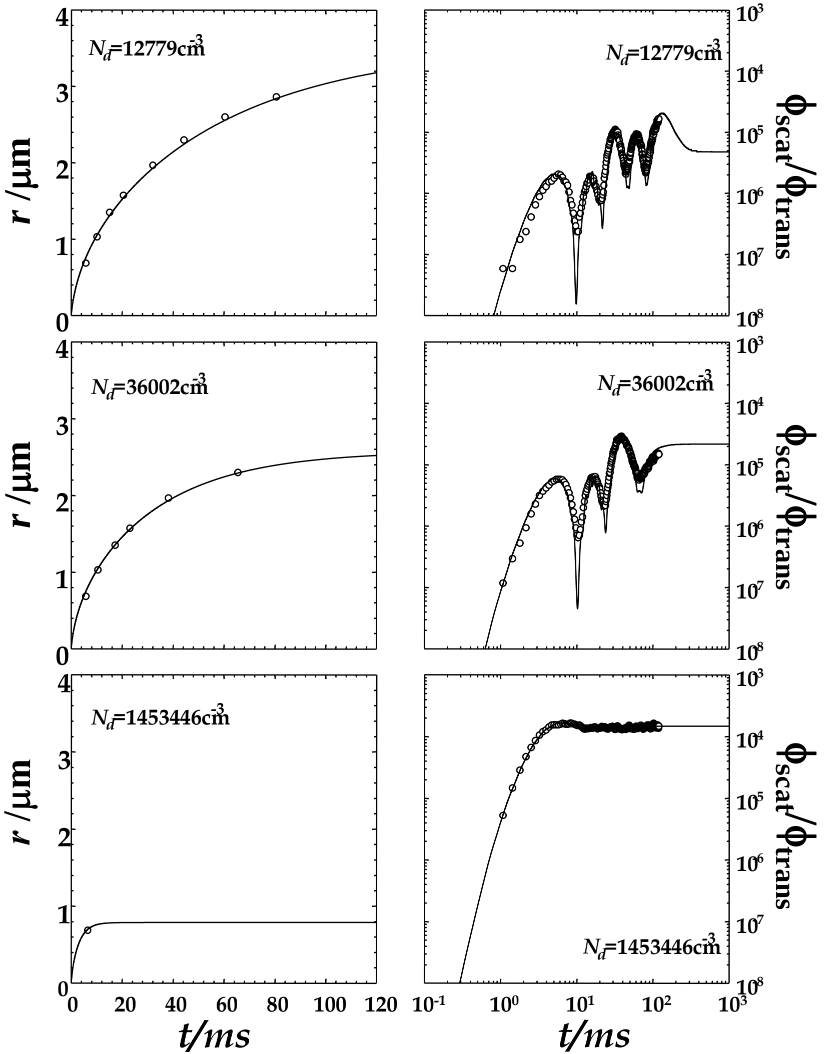
Nukleationspulskammer





CAMS: P. E. Wagner, J. Colloid Interface Sci. 105, 456 (1985)

Nukleationspulskammer

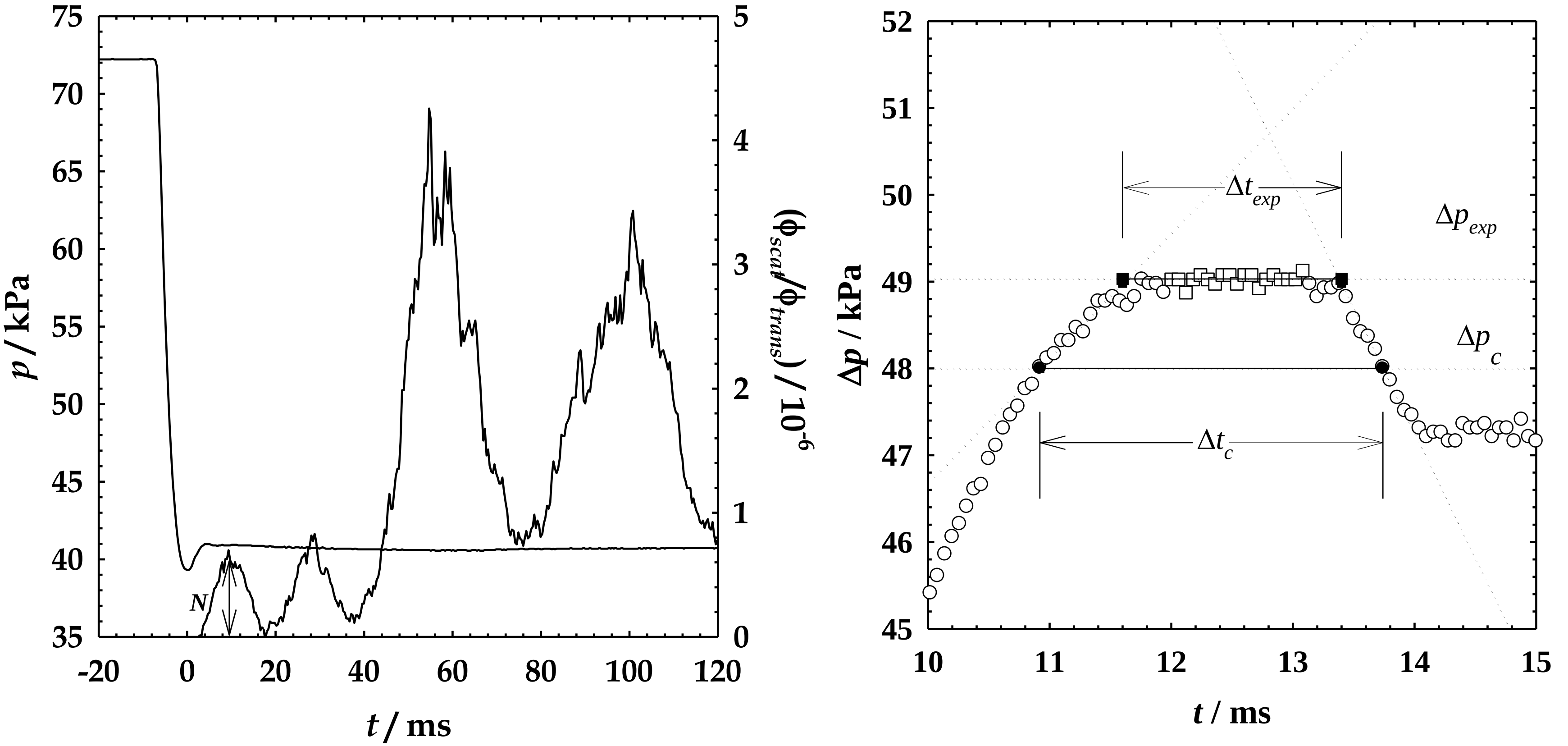


○ growth experiments by Fladerer (2002)

— theory by Fuchs-Sutugin (1971)

A.Fladerer, M. Kulmala, and R. Strey, J. Aerosol Sci. 33, 391 (2002)

Nukleationspulskammer



Höhe des ersten Mie-Maximums ⇒ Teilchenzahldichte *N*

Pulsevaluierung ⇒ Pulslänge $\Delta t \approx 1$ ms

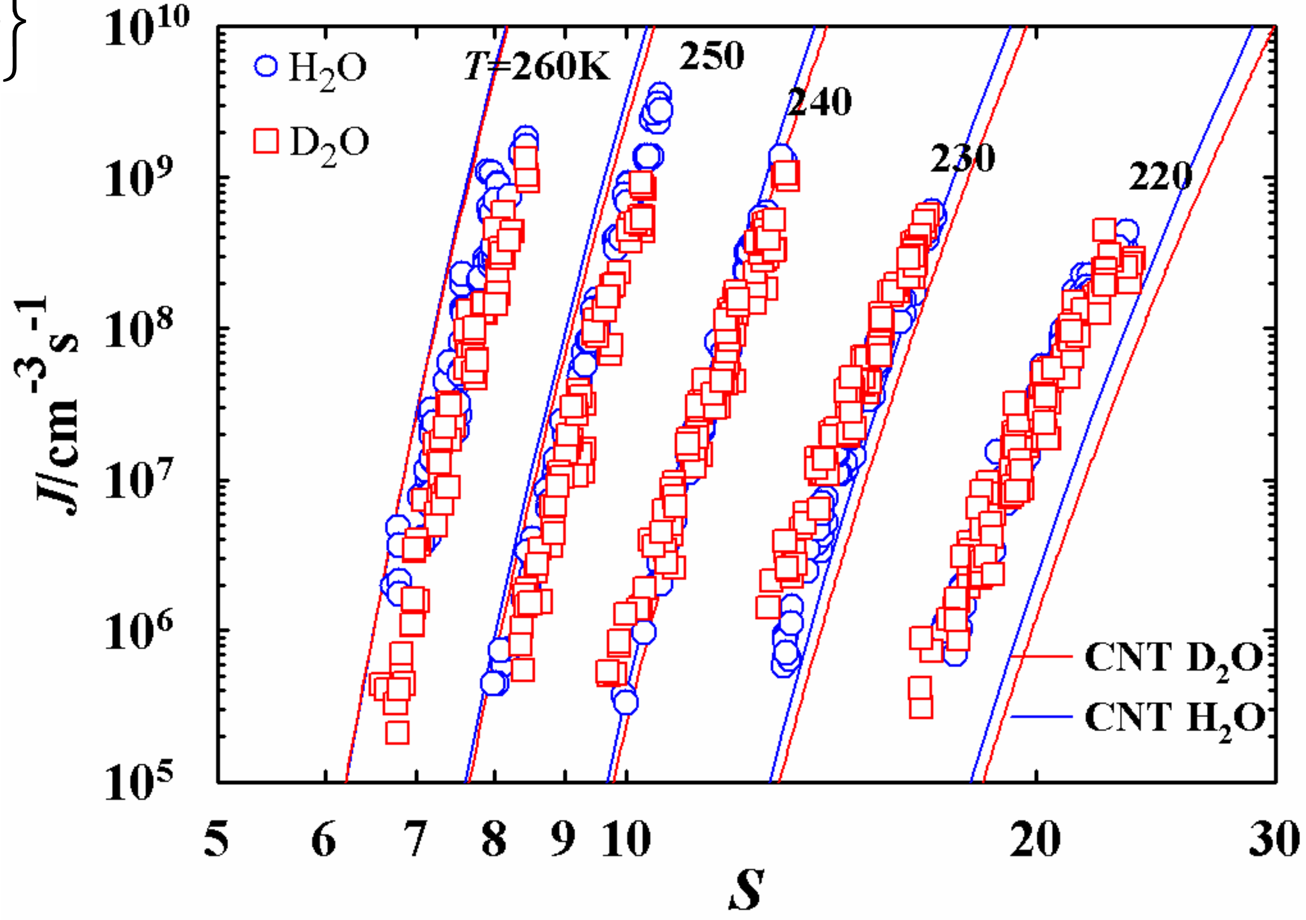
$$J = \frac{N}{\Delta t}$$

CAMS: P. E. Wagner, J. Colloid Interface Sci. 105, 456 (1985)

Keimbildungsraten / Wasser

$$J_{\mathrm{CNT}} = K \exp\left\{-\frac{\Delta G^*}{kT}\right\}$$

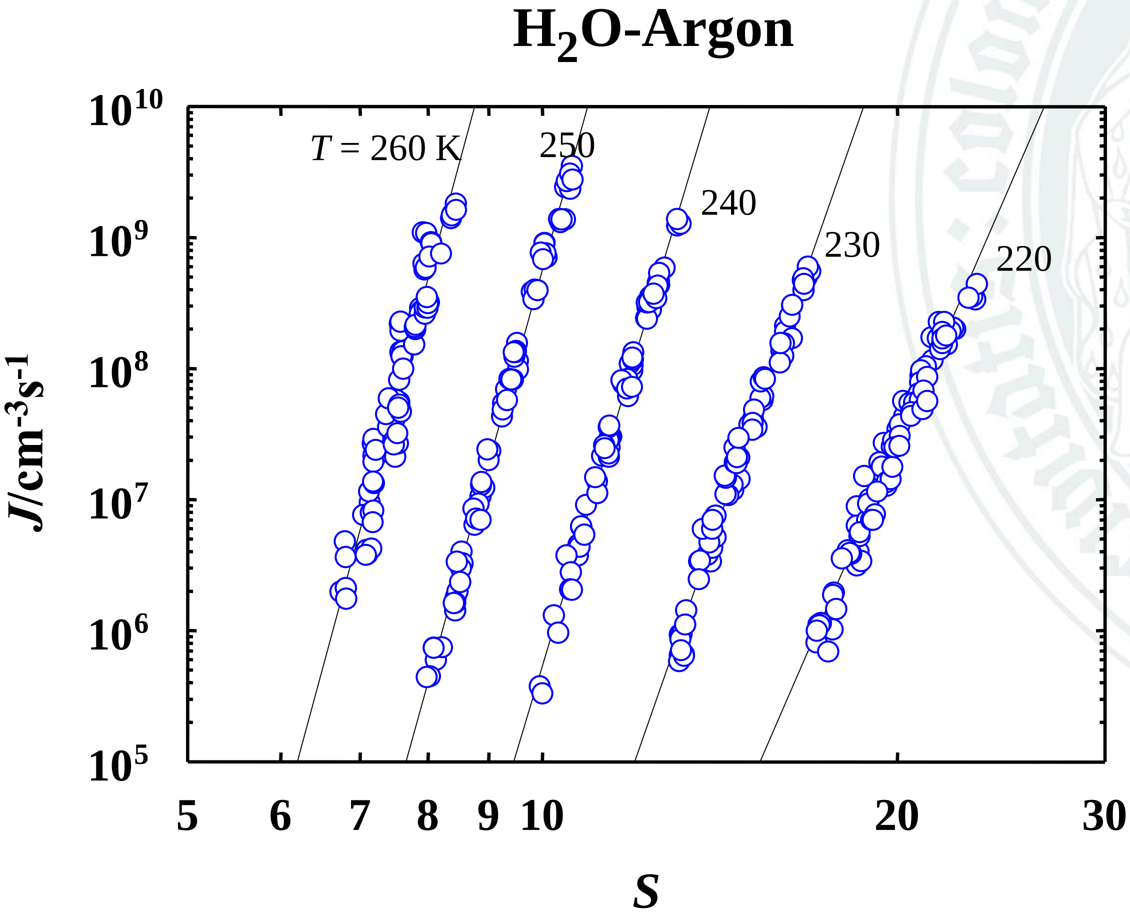
K = kinetic prefactor
ΔG^* = work of formation



J. Wölk, R. Strey, *J. Phys. Chem.* **105**, 11683, (2001)

Becker, R., and Döring, W., *Ann. Phys.* **24**, pp. 719 (1935).

Keimbildungsraten / Wasser



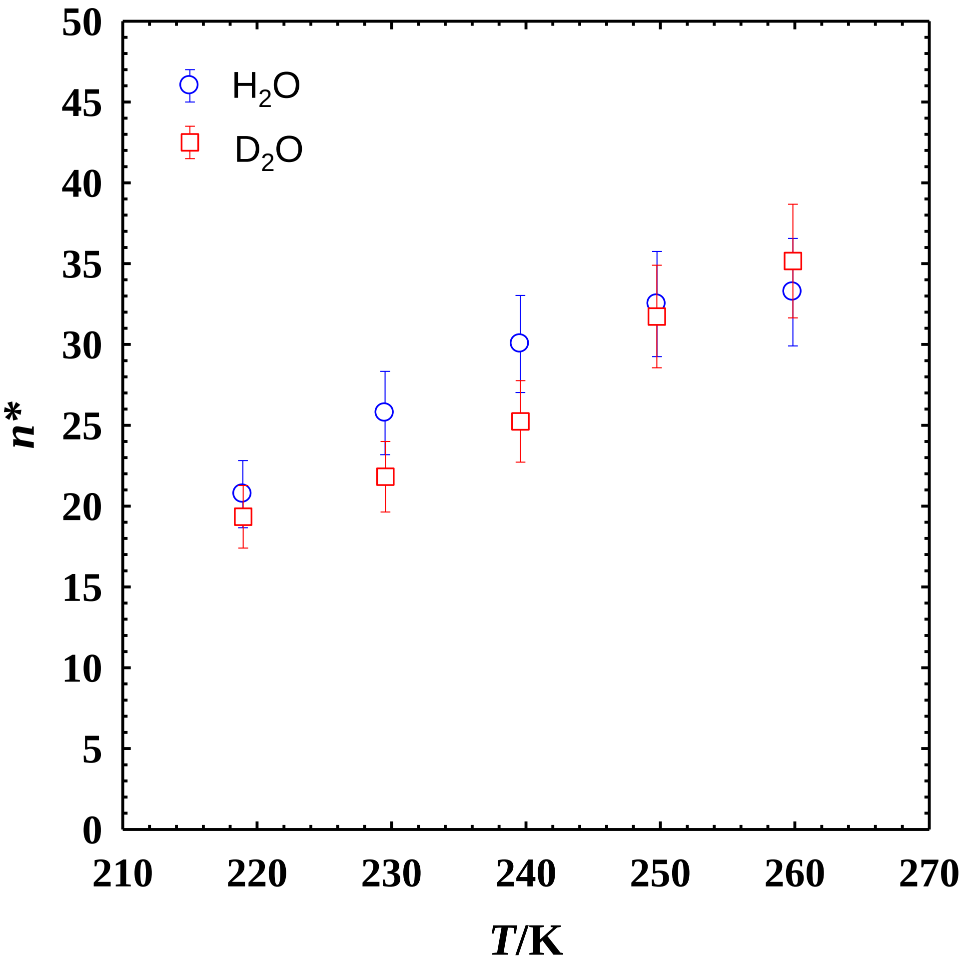
Kashchiev-Theorem:

$$\left.\frac{\partial \ln J}{\partial \ln S}\right|_T \cong n^*$$

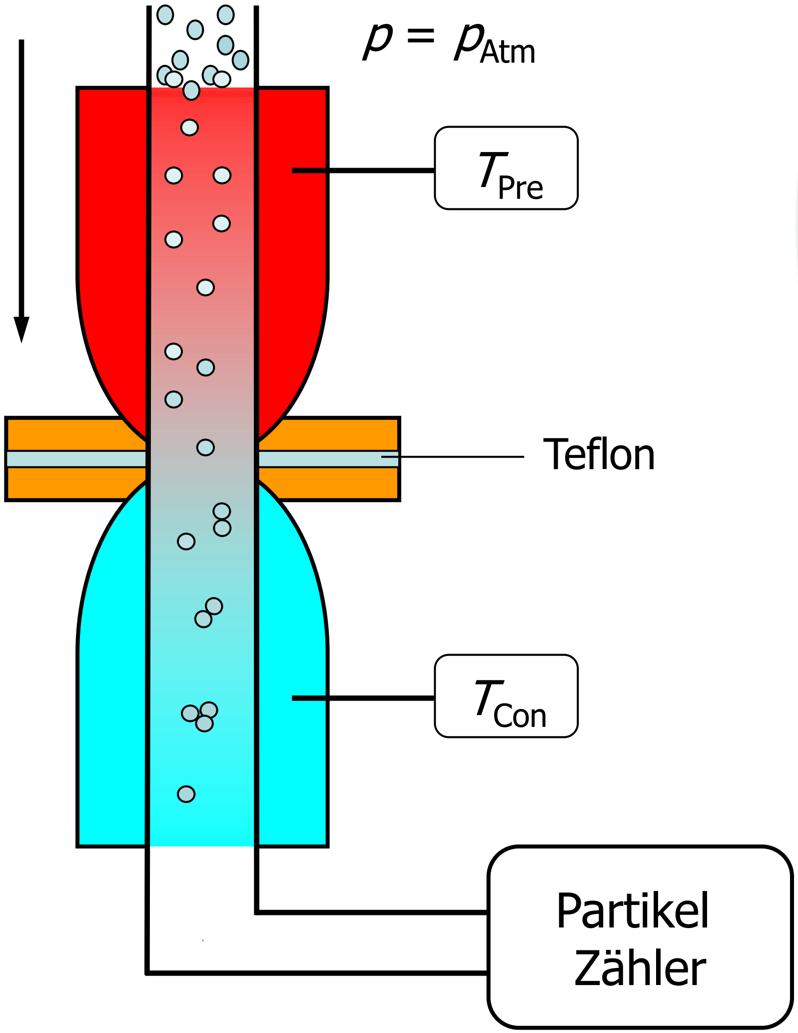
J. Wölk and R. Strey, J. Phys. Chem. B, 105, 11683 (2001)

D. Kashchiev, J. Chem. Phys. 76, 5098 (1982)

Kritische Clustergröße



Laminar flow diffusion chamber - LFDC



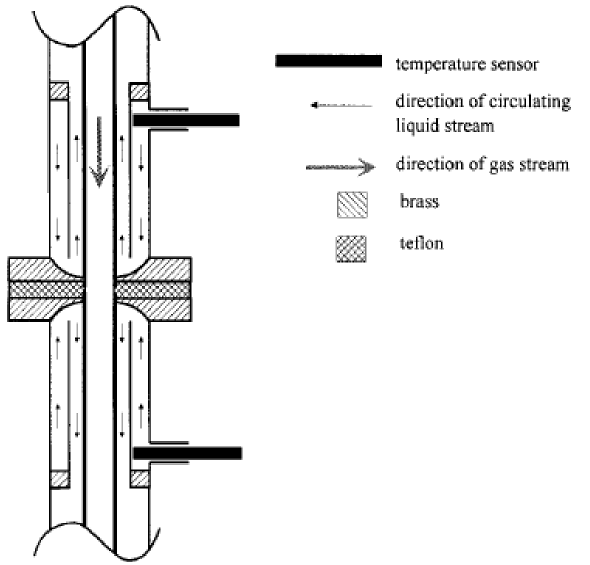


Figure 2. Schematic cross section of the connection between preheater and the condenser.

- **Partikel Zähler:**
  → Zahl der Teilchen /Zeit $N^* = \dfrac{n}{\Delta t}$
- **ΔV → nicht definiert**

H. Lhihavaninen Y. Viisanen, J.Phys.Chem. B, **105**,11619, 2001
A. Manka, Promotionsvortrag, Universität zu Köln, 2011

LFDC: experimentelle Keimbildungsrate

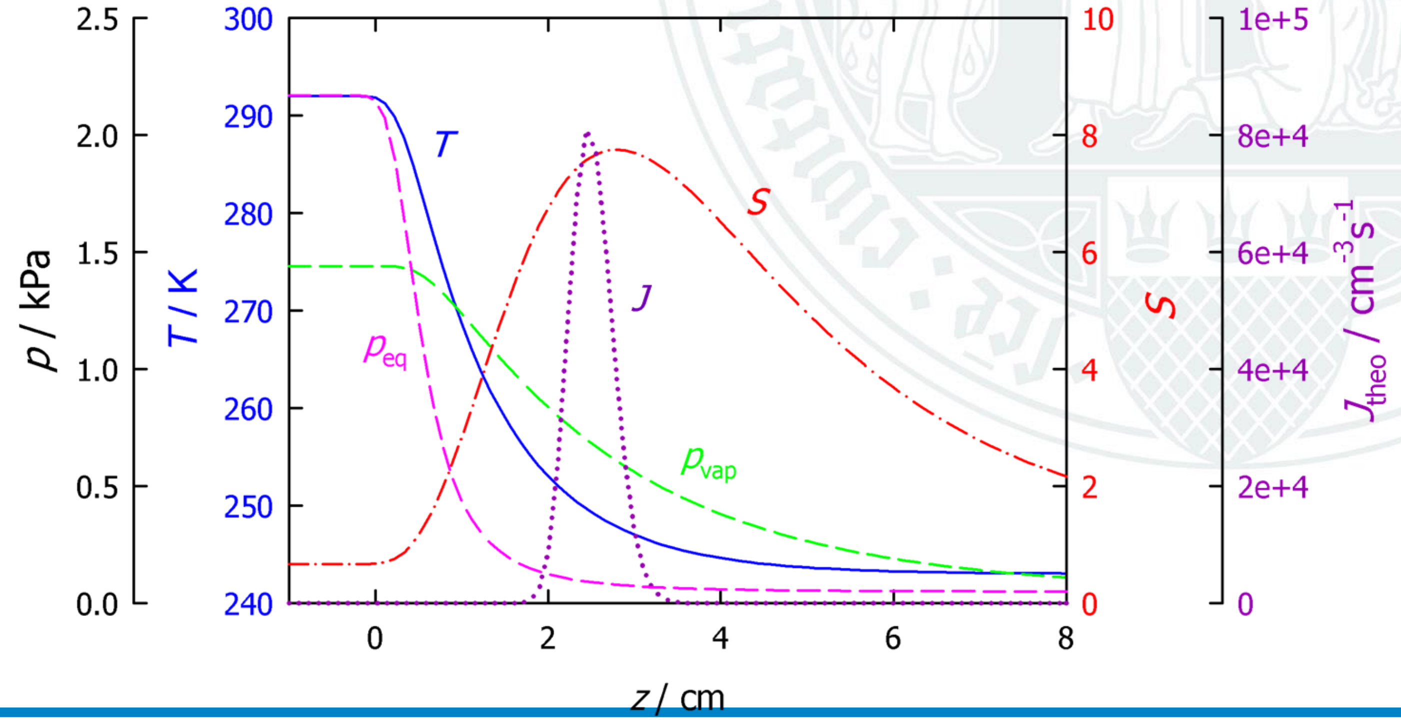
$$J = \frac{n}{\Delta t \Delta V}$$

$$\frac{J_{\exp}^{\max}}{\int J_{\exp} dV} = \frac{J_{theo}^{\max}}{\int J_{theo} dV}$$

$$N^* = \frac{n}{\Delta T}$$

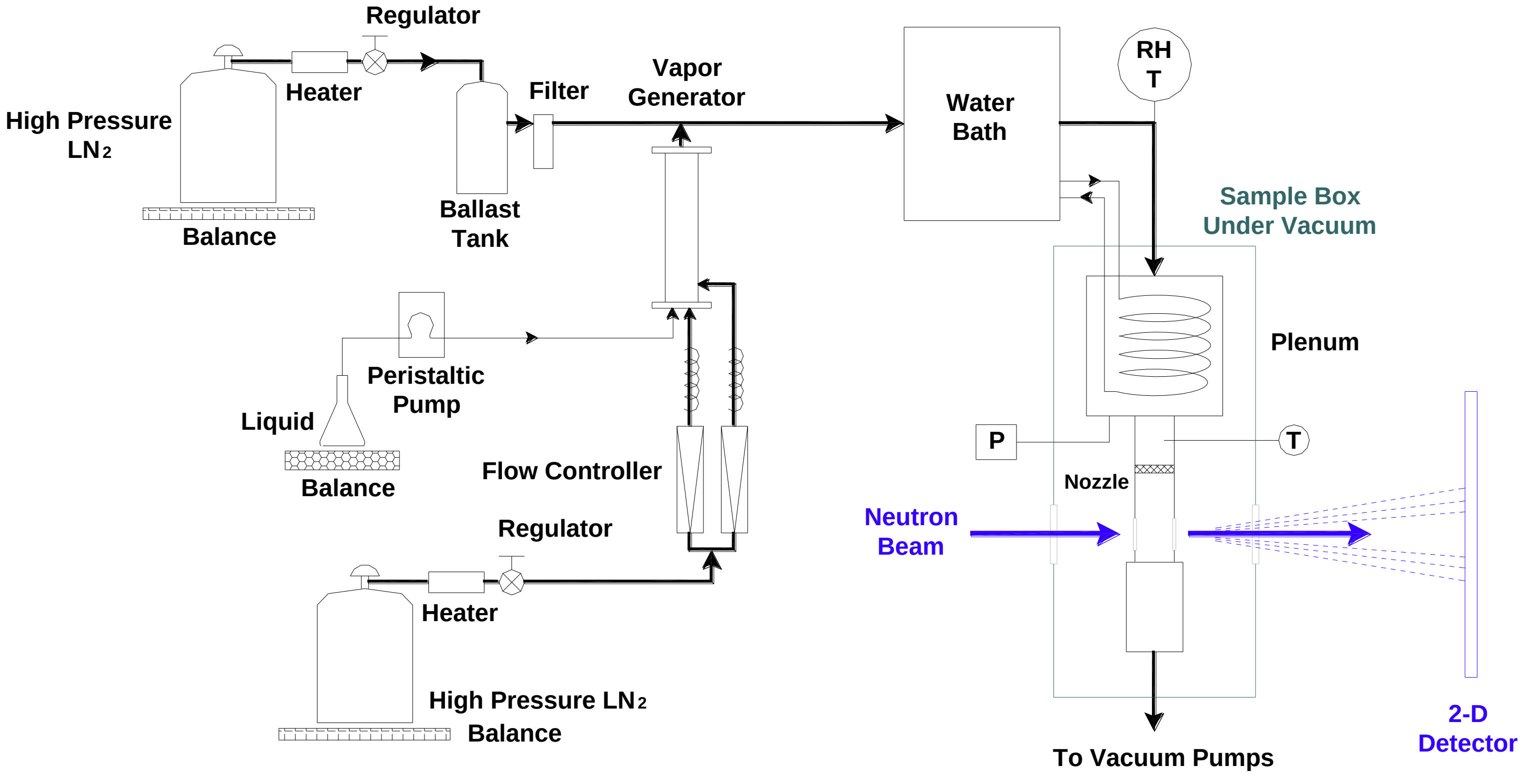
$$J_{\exp}^{\max} = \frac{J_{theo}^{\max}}{\int J_{theo} dV} \int J_{\exp} dV$$

$$\frac{1}{\Delta V}$$



A. Hyvärinen *et al*., *J. Chem. Phys*. 120, 24 (2004)

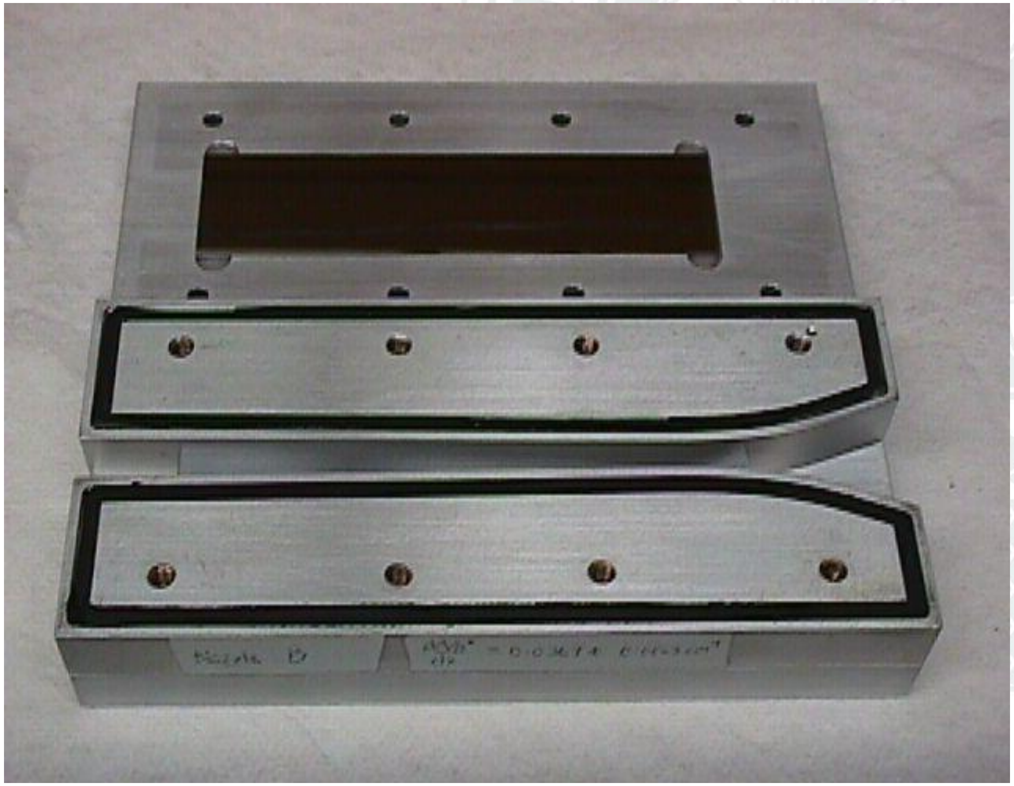
Überschalldüse



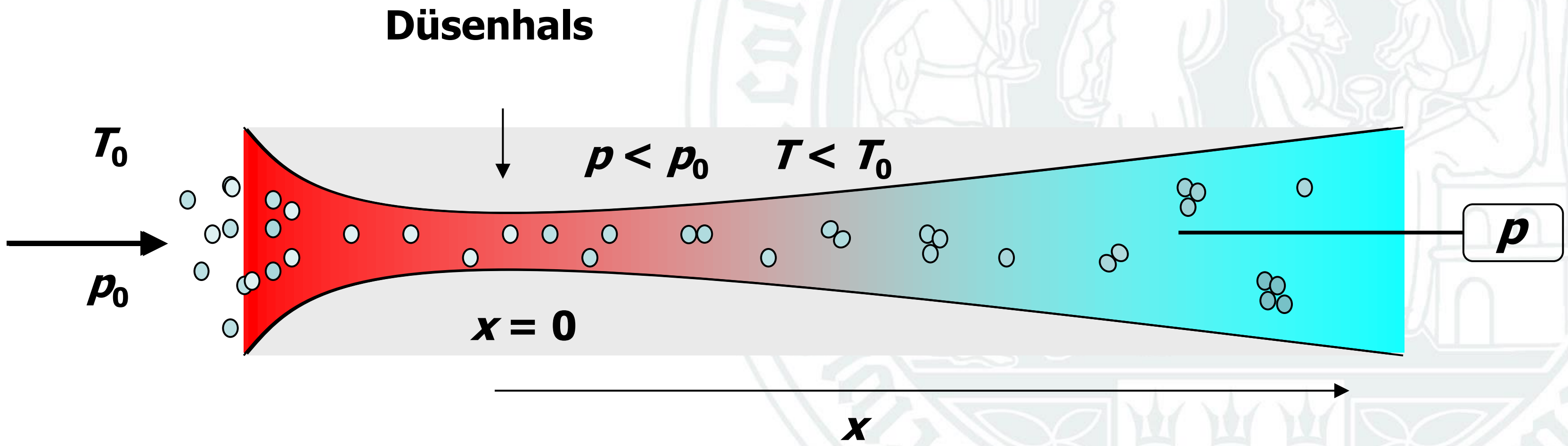
P - Pressure   T - Temperature   RH - Relative Humidity   - Heating Tape

Kim Y.J., Wyslouzil B.E., Wölk J., Strey R., AAAR (2002).

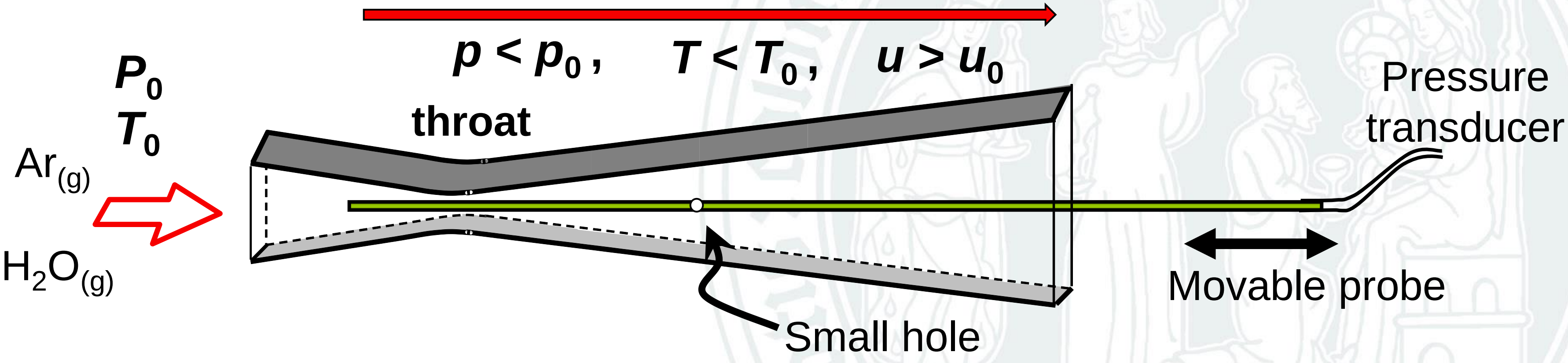
Überschalldüse



Überschalldüse



Überschalldüse



… Lots of carrier gas; <2% condensible

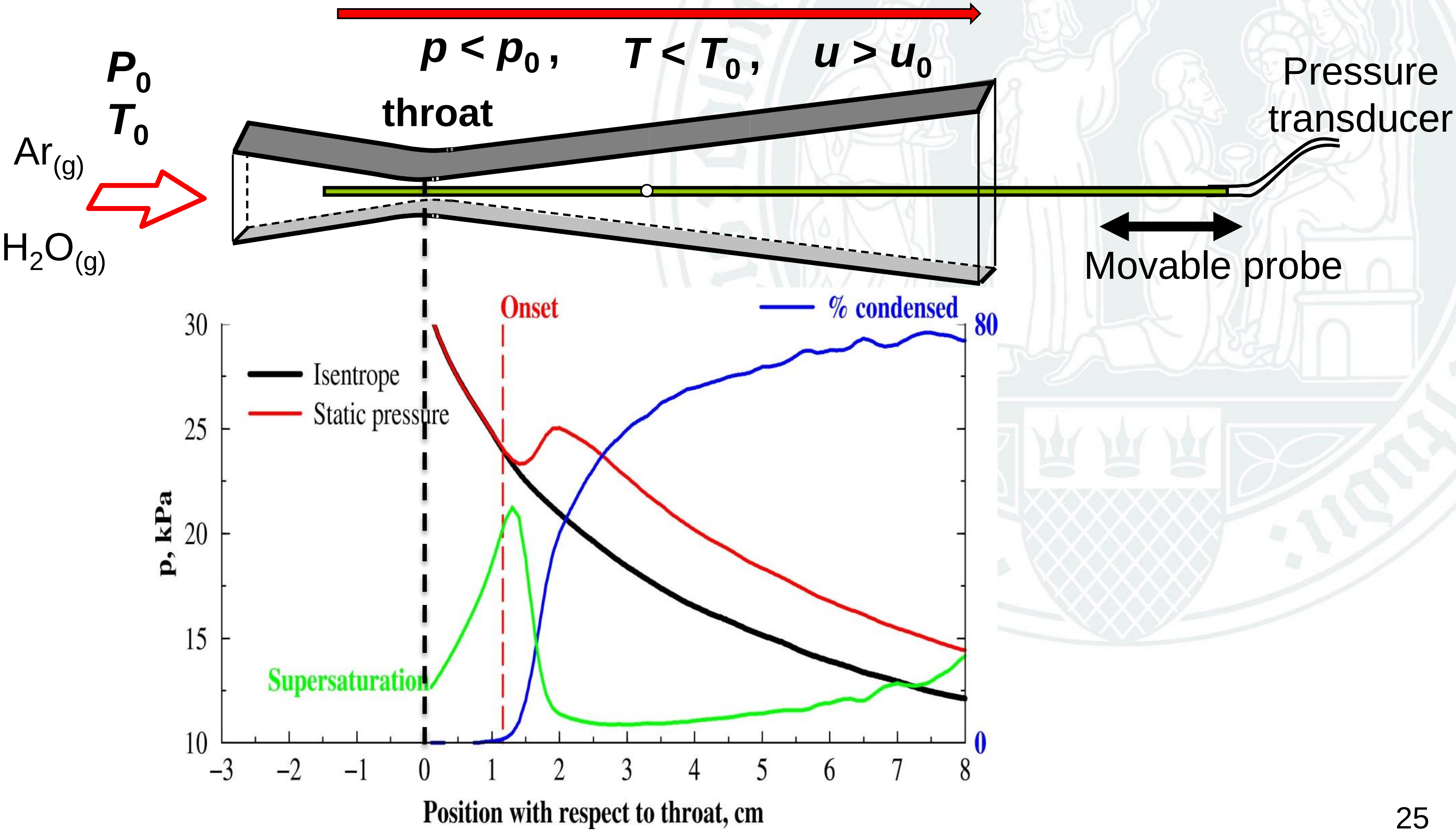
u ~ 400 m/s **$\Delta x/u = \Delta t$** **1 mm ~ 2.5 µs**

gemessen
- Anfangsdruck
- Anfangstemperatur
- Gasphasenzusammensetzung

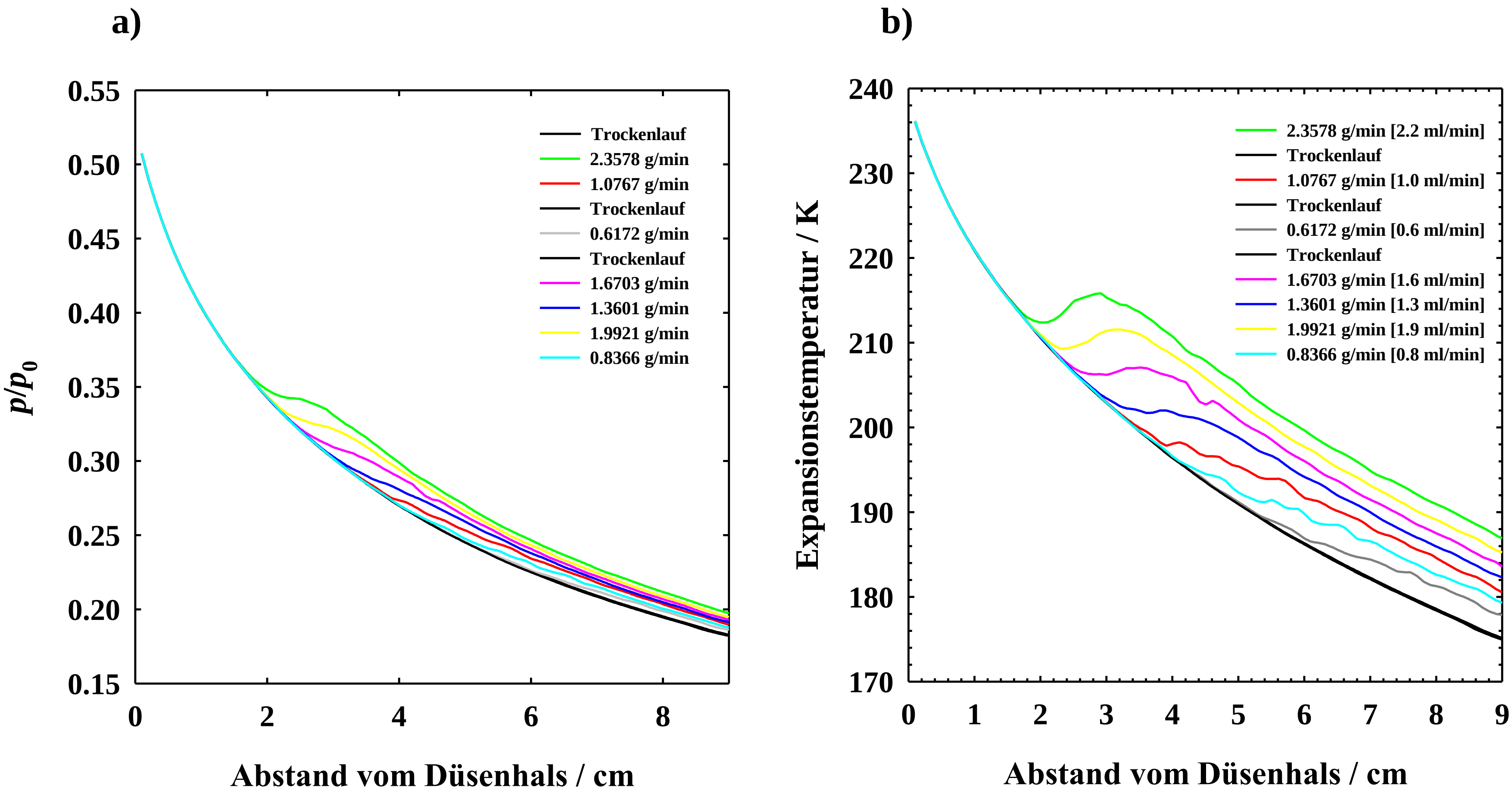
gemessen
- statischer Druck

Berechnet:
- Kondensationsmenge

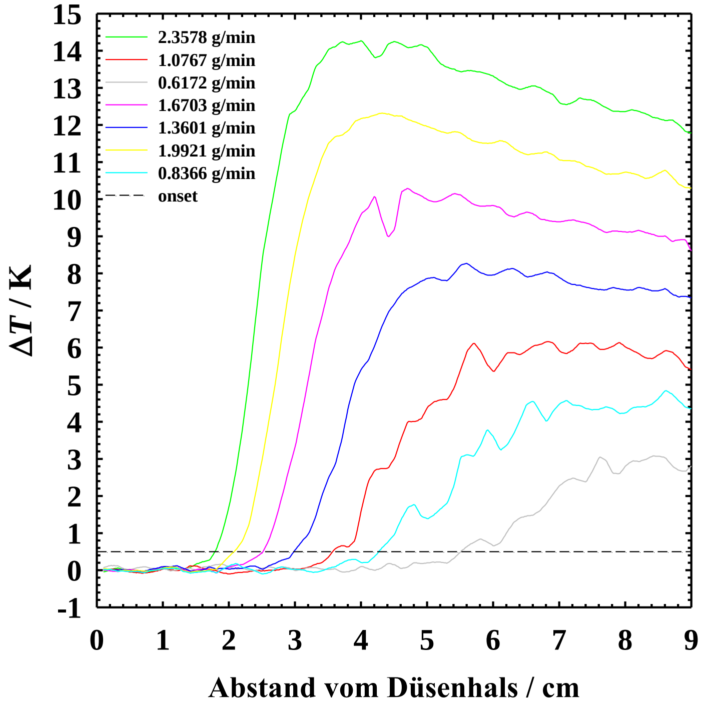
Supersonic Nozzle

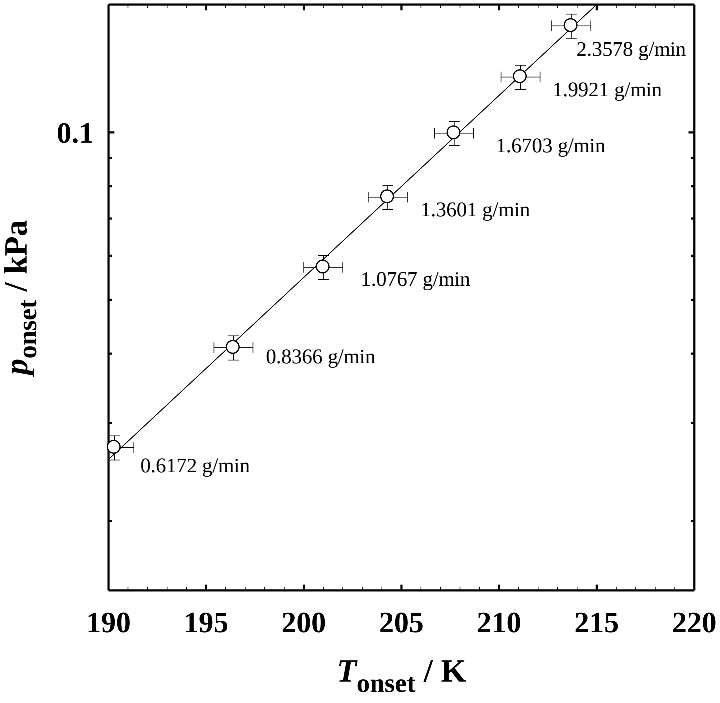


Überschalldüse

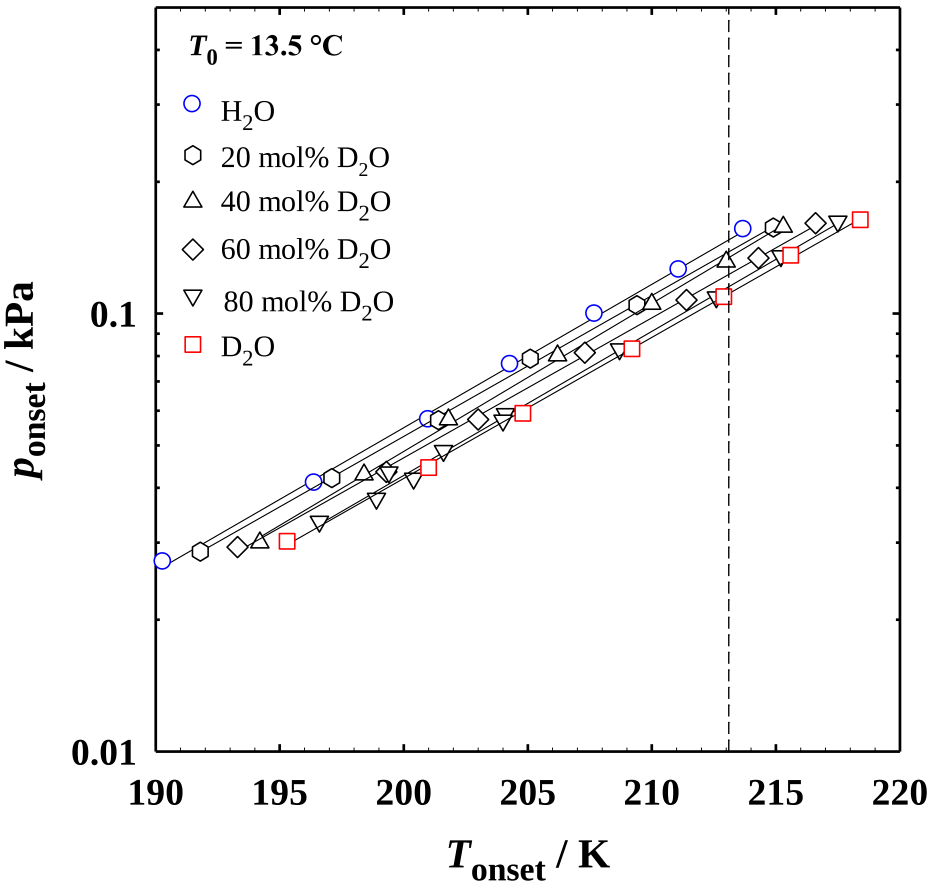


Überschalldüse

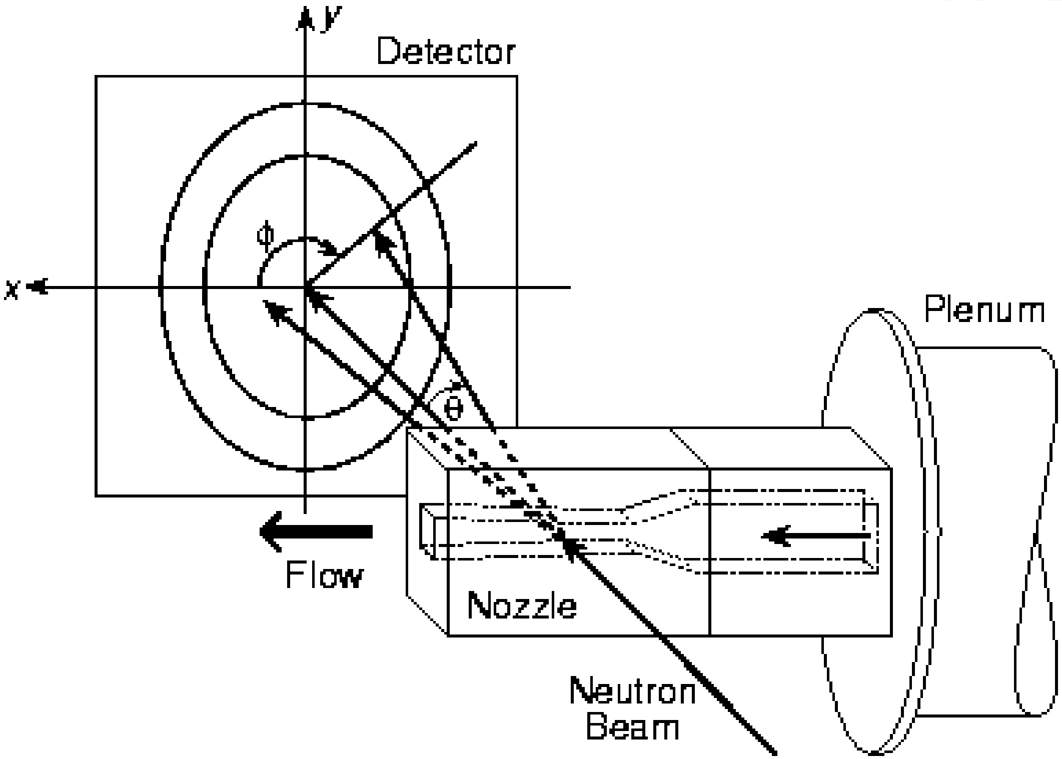


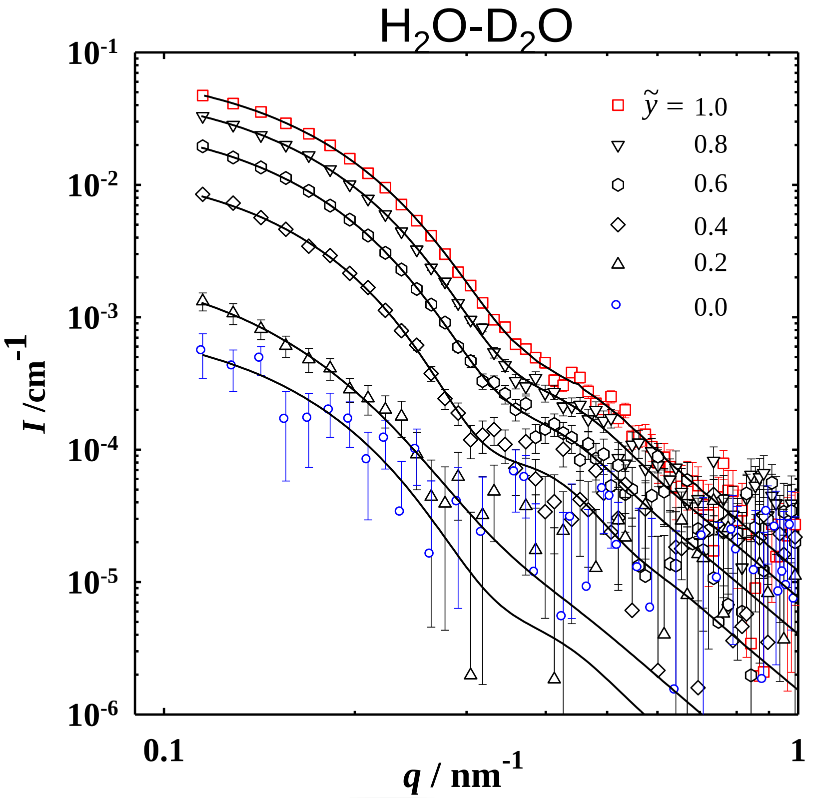


Überschalldüse



Überschalldüse - SANS





θ : scattering angle

q : scattering vector

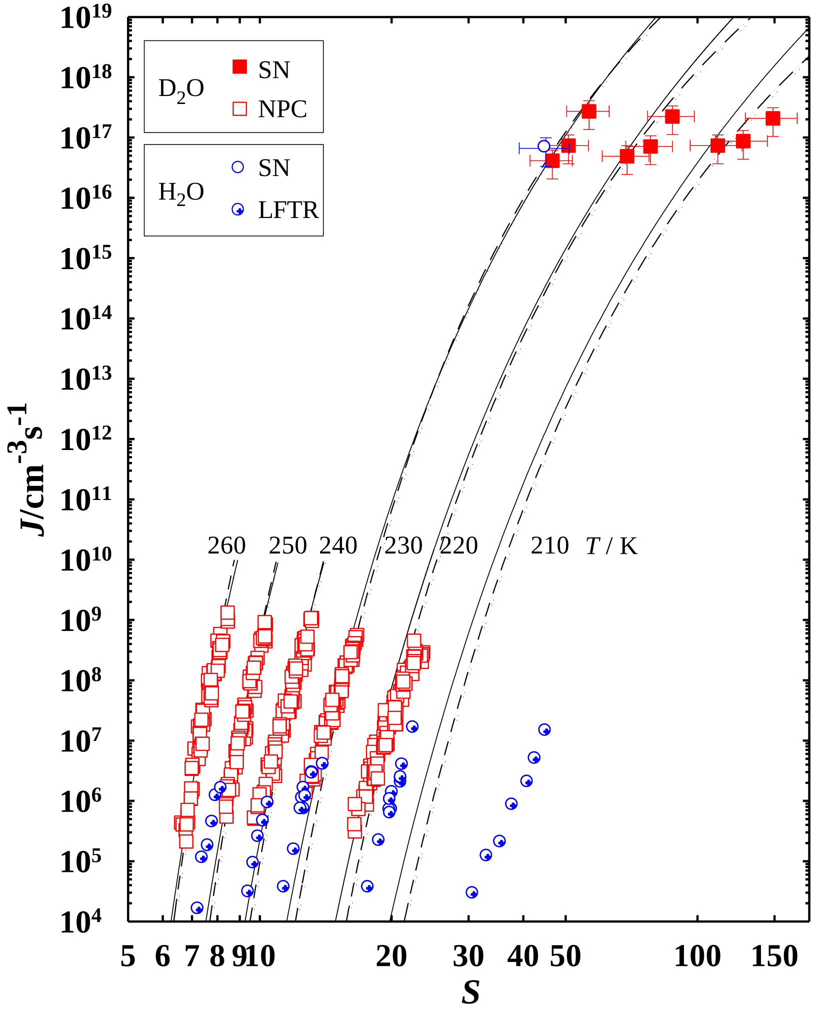
λ : wavelength (λ = 0.8 nm)

$N \approx 2\text{x}10^{11}$ cm^{-3} $r \approx 13$ nm

B.E. Wyslouzil, J.L. Cheung, G. Wilemski, and R. Strey, Phys. Rev. Lett. 79, 431 (1997)
C.H. Heath, K. Streletzky, B.E. Wyslouzil, J. Wölk and R. Strey,
J. Chem. Phys. 118, 5465 (2003)

Keimbildungsraten

—— J_{corr}



Mikheev, V.B.; Irving, P.M.; Laulainen, N.S.; Barlow, S.E.; Pervukhin, V.V. J. Chem. Phys. 116, 10772 (2002)

J. Wölk and R. Strey, J. Phys. Chem. B, 105, 11683 (2001)

Kim Y.J. Wyslouzil B.E. Wilemski G. Wölk J. Strey R. J. Phys. Chem. A 108, 4365 (2004)

CAMS-SANS-SAXS

- Nukleationspulskammer und Überschalldüse liefern Keimbildungsraten

- Verwendete Streumethoden:

CAMS:

- 200 nm - 3 µm
- geringe Anzahldichte

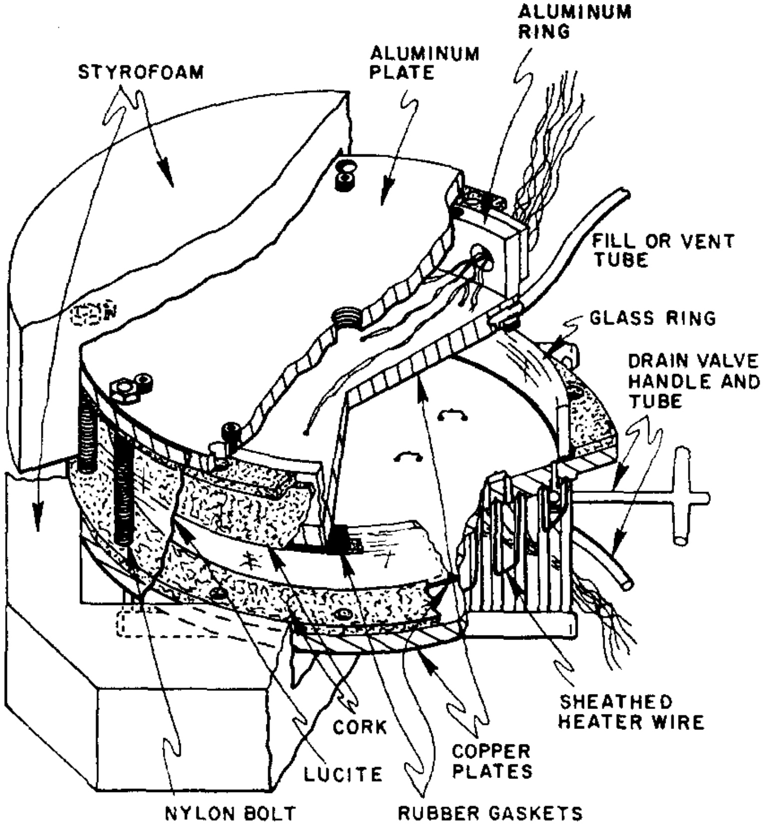
SANS:

- 1-200 nm
- hohe Anzahldichte
- Kontrastierung möglich

SAXS:

- 0.1-50 nm
- hohe Anzahldichte
- hohe Intensität
- exakte Wellenlänge
- APS: Punktgeometrie

Diffusionsnebelkammer



4 STRANDS OF NICHROME HEATER WIRE ON OUTSIDE OF GLASS RING OMITTED FOR CLARITY.

FIG. 2. Cutaway view of diffusion cloud chamber.

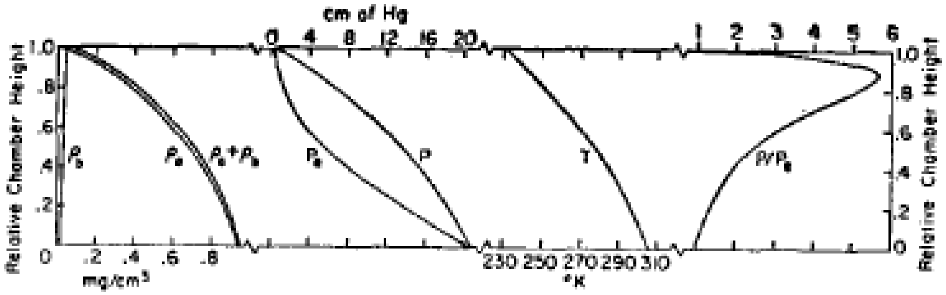


FIG. 1. Variation with height of the mass densities of the carrier gas ρ_b and the vapor ρ_a, the equilibrium vapor pressure P_e, the partial pressure of the vapor P, the temperature T, and the supersaturation P/P_e. Illustrated with data from hexane point 6.

J.L.Katz, B.J.Ostermier, J.Chem.Phys. **47**, Issue 2, pp. 478-487 1967

single piston exp. chamber

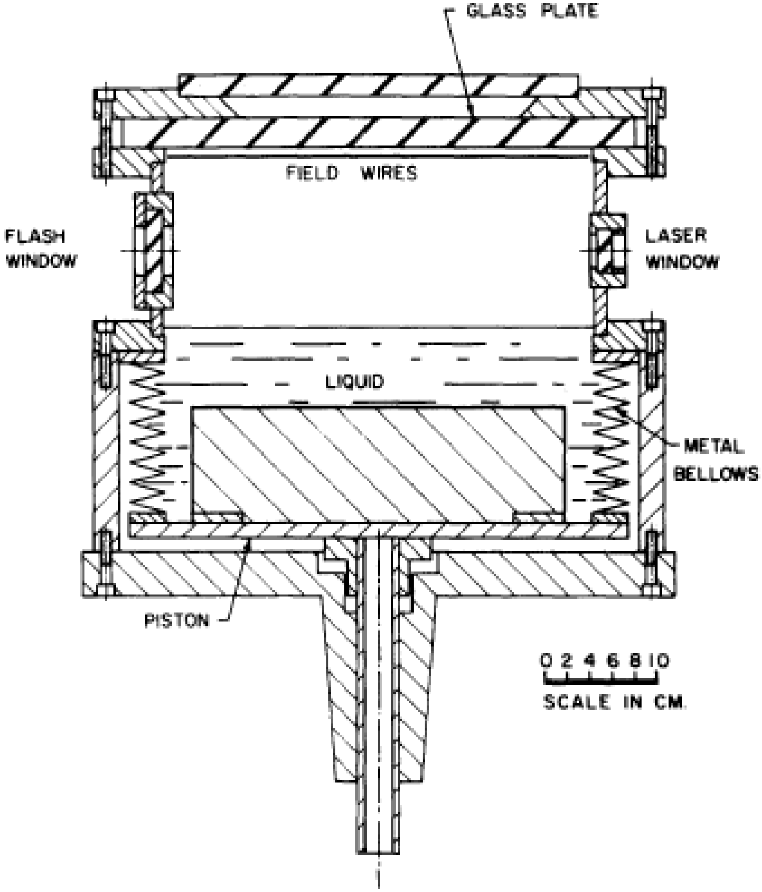


FIG. 1. Schematic diagram of the cloud chamber.

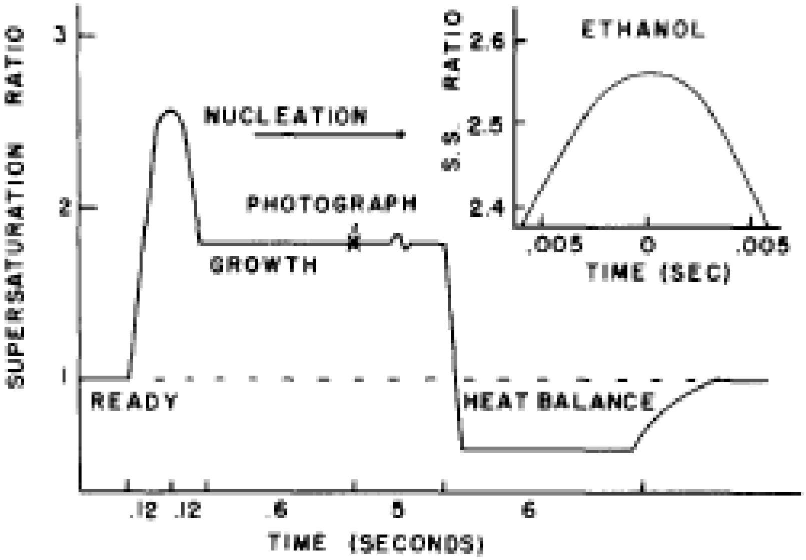


FIG. 2. Typical chamber expansion cycle for ethanol. The inset graph shows the shape of the nucleation pulse. See the text for an explicit expression for the pulse as a function of time and pressure.

J. L. Schmitt, Rev. Sci. Instrum. **52**, 1749 (1981).

piston expansion wave tube

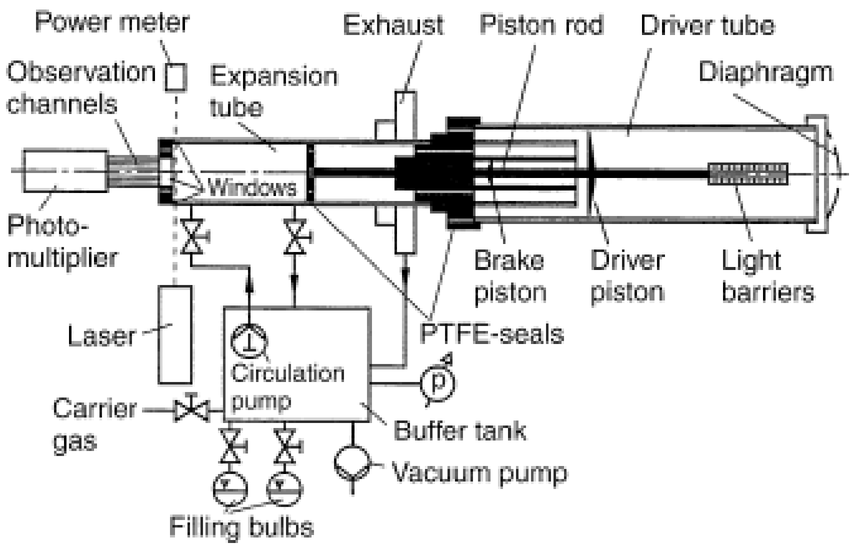
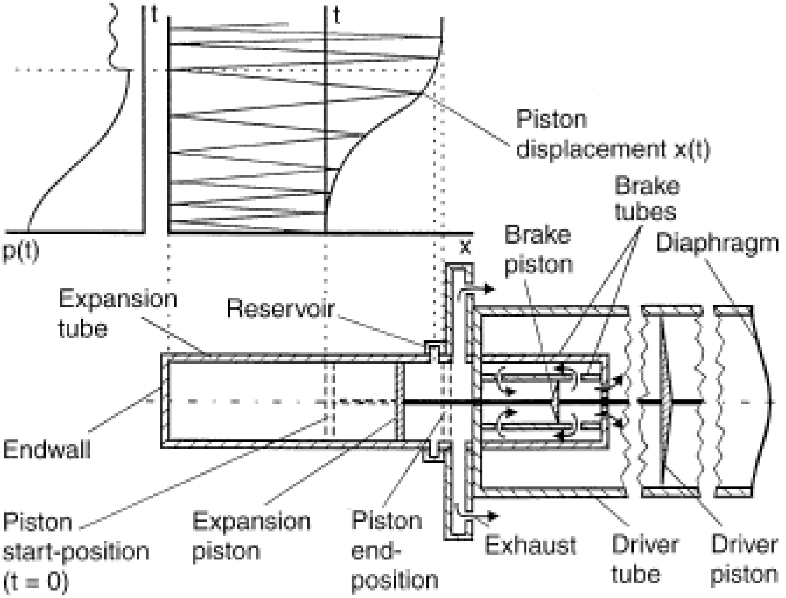
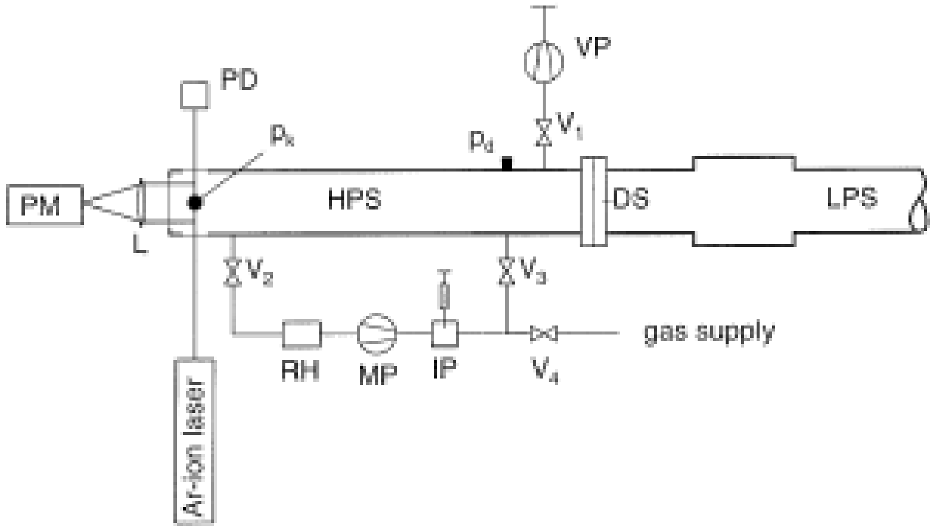


Fig. 2. Schematic of the pex-tube set-up



F. Peters, T. Rodemann, Experiments in Fluids **24**, 300, 1998.

pulse expansion wave tube



HPS	high pressure section	$V_{1,...,4}$	valves
LPS	low pressure section	VP	vacuum pump
DS	diaphragm section	MP	mixing pump
PM	photomultiplier	IP	injection point
PD	photodiode	p_d	static pressure (Druck PDCR 200
L	lens	p_k	dynamic pressure (Kistler 603 B)
RH	humicap (HMP 124B)		

Fig. 6. Pulse-expansion wave tube setup

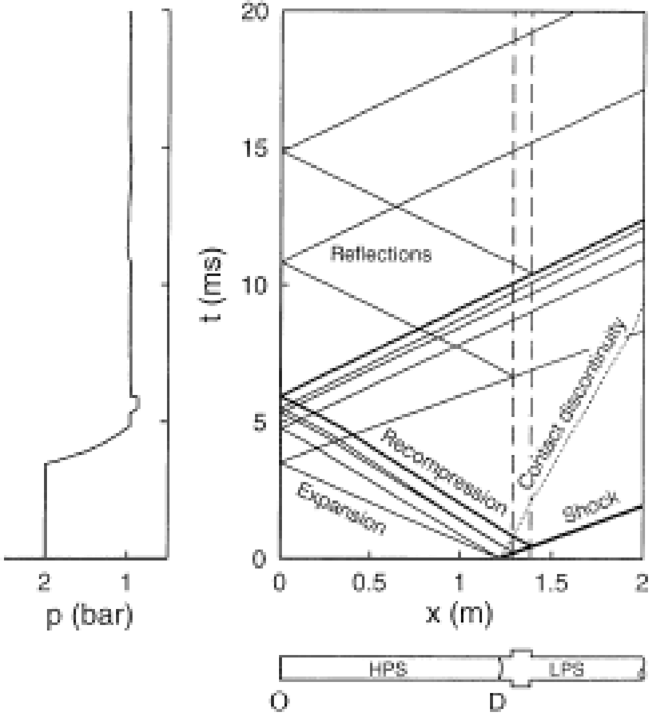


Fig. 2. x–t diagram of the wave pattern in the pulse-expansion wave tube with schematic tube configuration and pressure versus time diagram. The dashed lines show the position of the local widening. A nucleation pulse is formed at the observation point O at the endwall of the HPS. D denotes the position of the diaphragm. The diagrams were calculated with the Random Choice numerical Method (RCM). The calculations were done with nitrogen gas, with pressures of 2 bar in the HPS, and 1 bar in the LPS

K.N.H.Looijmans, M.E.H. van Dongen, Experiments in Fluids, **23**, 54, 1997.

pulse expansion wave tube

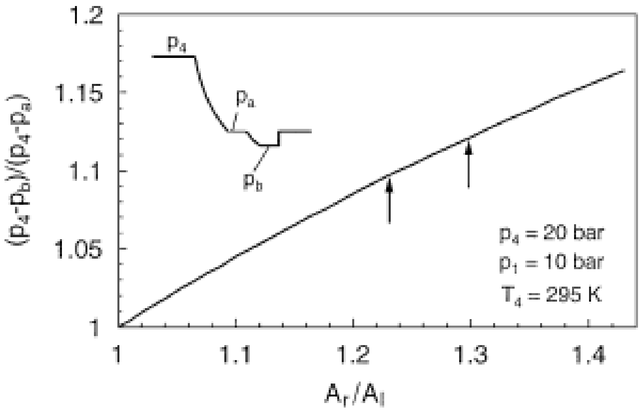


Fig. 4. Depth of the nucleation pulse compared to the initial expansion, as a function of the ratio of the cross-sectional areas (A_r) and (A_l). The initial conditions of the HPS are listed in the figure. The gas was methane in both the HPS and LPS. The arrows indicate the ratios of the cross-sectional areas used in the nucleation experiments

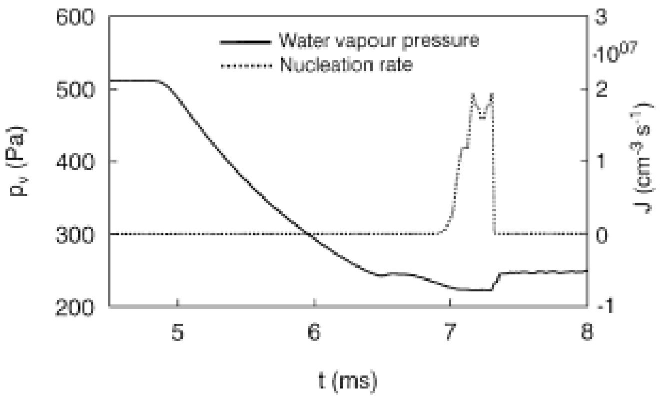
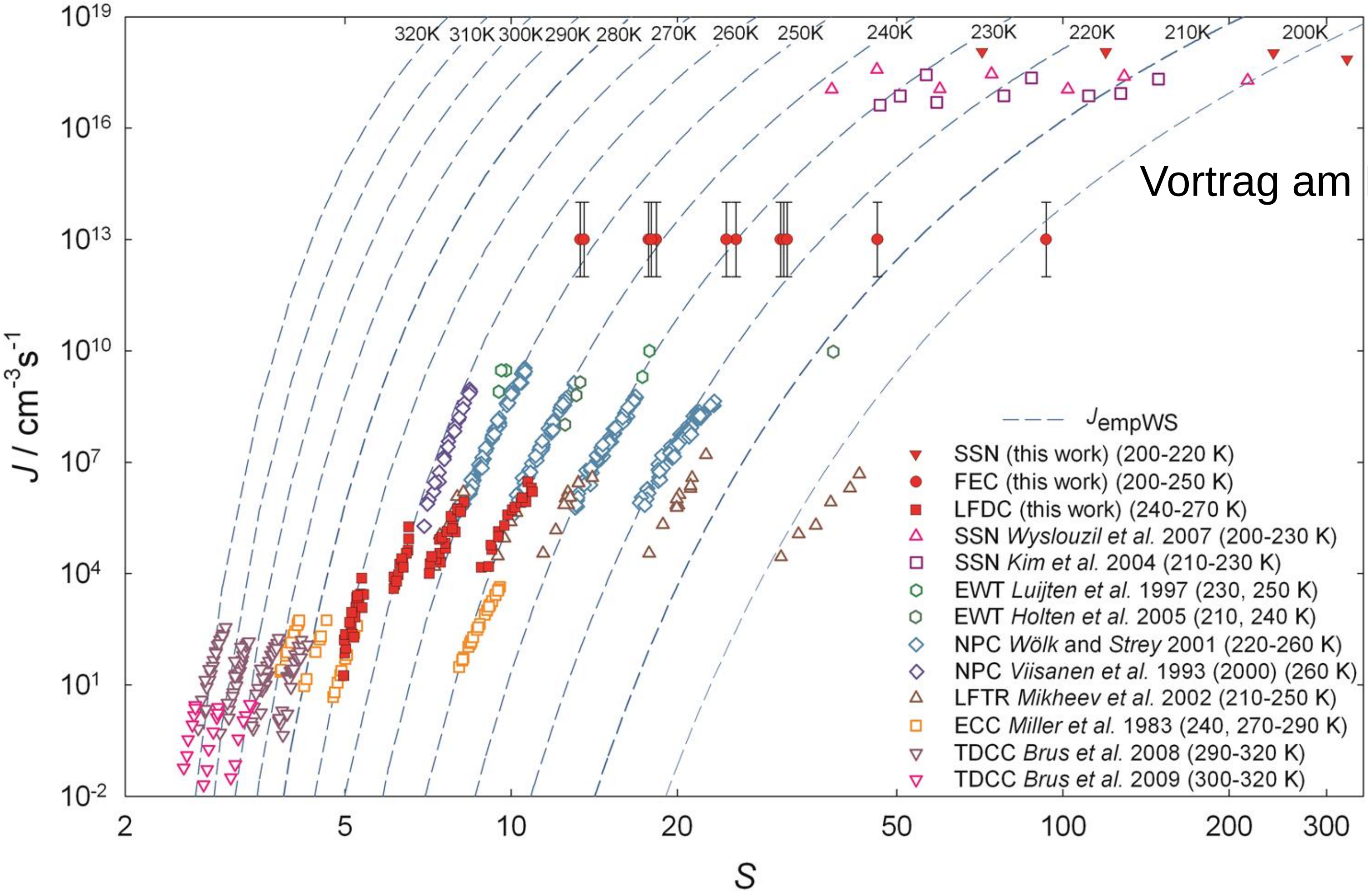


Fig. 5. Simulation of the nucleation rate by classical nucleation theory for water vapour during the nucleation pulse. The pressure history is taken from an experimental run

K.N.H.Looijmans, M.E.H. van Dongen, Experiments in Fluids, **23**, 54, 1997.

Keimbildungsraten

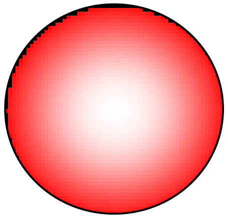


Vortrag am Donnerstag

A. Manka, Doktorarbeit , Universität zu Köln (2011)

Theorie

classical nucleation theory



$$J = K\exp\left\{-\frac{\Delta G^*}{kT}\right\}$$

K = kinetischer Vorfaktor

ΔG^* = Keimbildungsarbeit

Annahmen:

1. sphärisch, inkompressibel, homogen mit scharfer Grenzfläche
2. Dampfphase verhält sich ideal
3. Flüssigkeit hat die gleiche thermodynamischen Eigenschaften (Grenzflächenspannung, Dichte, Dampfdruck) wie eine flache bulk-Phase

R. Becker und W. Döring, Ann. Phys., **24**, 719 (1935)

Theorie - CNT

$$\Delta G(n) = G(n) - G(0)$$

$G(n)$ freie Gibb‘s - Enthalpie eines Systems bestehend aus Dampfphase und einem Tropfen der Größe *n*

$G(0)$ freie Gibb‘s - Enthalpie der reinen Dampfphase

Von der Thermodynamik wissen wir, dass die freie Gibb‘s – Enthalpie gegeben ist mit:

$$G(p,T,N) = U\text{-}TS+pV = \mu N$$

Für die reine Dampfphase gilt somit:

$$G(0) = \mu_v N$$

Theorie - CNT

Die freie Gibb‘s - Enthalpie *G(n)* eines Systems bestehend aus einer Dampfphase und einem Tropfen der Größe *n* ist gegeben durch:

$$G(n)=\mu_v N_v+\mu_l n+\sigma A$$

mit $\Delta G(n)=G(n)-G(0)$

⇨
$$\begin{aligned}\Delta G(n) &= \mu_v N_v+\mu_l n+\sigma A-\mu_v N \qquad N=N_v+n\\ &= \mu_v(N-n)+\mu_l n+\sigma A-\mu_v N\\ &= -\mu_v n+\mu_l n+\sigma A\end{aligned}$$

$$\Delta G(n) = -n\Delta\mu+\sigma A \qquad \Delta\mu = \mu_v-\mu_l$$

Theorie - CNT

Evaluierung von $\Delta\mu$:

Gibbs-Duhem Gleichung bei konstanter Temperatur: $N d\mu_v = V dp_v$

Annahme - Dampf verhält sich ideal: $p_v = NkT / V$ $V/N = kT/p_v$

$$d\mu_v = \frac{V}{N} dp_v = kT \frac{dp_v}{p_v}$$

$$\Rightarrow \int_{\mu_v^{eq}}^{\mu_v} d\mu_v = kT \int_{p_v^{eq}}^{p_v} \frac{dp_v}{p_v}$$

$$\Rightarrow \mu_v(p_v) - \mu_v^{eq}\left(p_v^{eq}\right) = kT \ln\left(p_v / p_v^{eq}\right)$$

Theorie - CNT

Für die Flüssigkeit mit Grenzfläche ist die Gibbs-Duhem Gleichung:

$$d\mu_l = \frac{V_l}{n} dp_l = v_l dp_l$$

v_l ist das molare Volumen der flüssigen Phase

Annahme: inkompressible Flüssigkeit: => v_l=const. wenn der Druck variiert

$$\Rightarrow \int_{\mu_l^{eq}\left(p_l^{eq}\right)}^{\mu_l(p_v)} d\mu_l = v_l \int_{p_l^{eq}}^{p_v} dp_l \Rightarrow \mu_l(p_v) - \mu_l^{eq}\left(p_v^{eq}\right) = v_l\left(p_v - p_l^{eq}\right)$$

Theorie - CNT

Im Gleichgewicht :

$$p_{eq} = p_v^{eq} = p_l^{eq}$$

$$\Delta\mu = \mu_v - \mu_l = kt\ln\left(p_v / p_{eq}\right) - v_l\left(p_v - p_{eq}\right) \qquad S = \frac{p_v}{p_{eq}}$$

$$\Rightarrow \Delta\mu = kt\ln S - v_l\, p_{eq}\left(S - 1\right)$$

$v_l\, p_{eq}\left(S - 1\right)$ Volumenterm, typischerweise sehr klein
=> vernachlässigbar

$$\boxed{\Rightarrow \Delta\mu = \boldsymbol{kt}\,\mathbf{ln}\,\boldsymbol{S}}$$

Theorie - CNT

Volumen eines inkompressiblen, flüssigen und sphärischen Tropfens:

$$V_l = nv_l = \frac{4\pi}{3} r_n^3$$

r_n= Radius eines Tropfens der Größe *n*

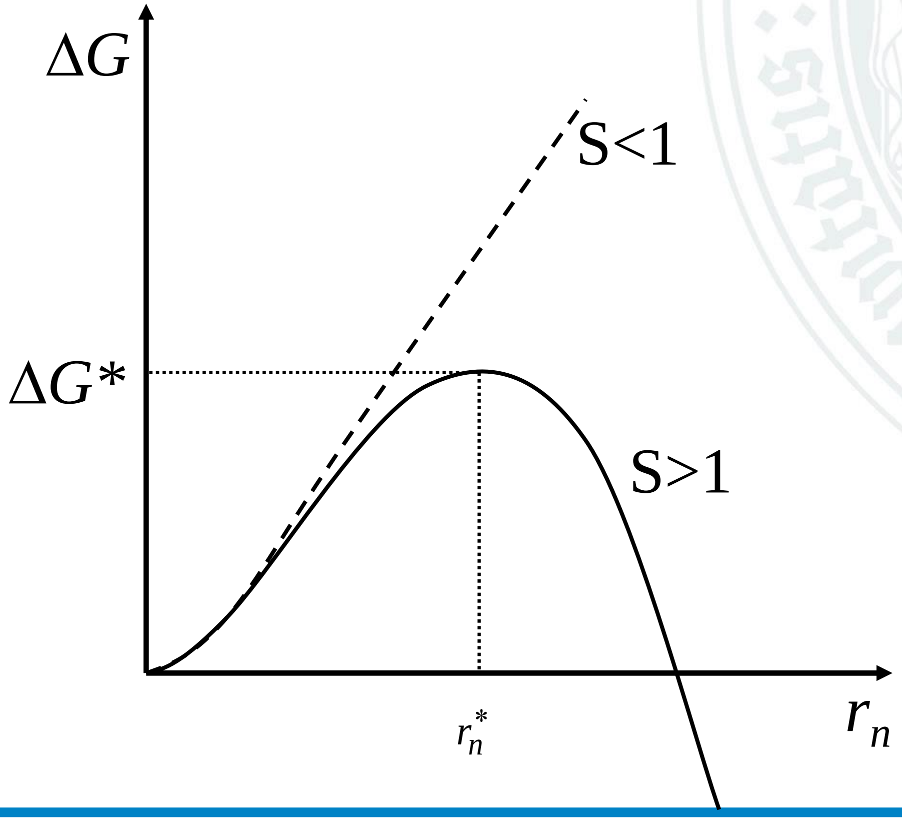
Oberfläche des Tropfens:

$$A = 4\pi r_n^2$$

$$\Delta G(n) \;=\; -n\Delta\mu + \sigma A = -\frac{4\pi r_n^3}{3v_l} kT \ln S + \sigma 4\pi r_n^2$$

Theorie - CNT

$$\Delta G(n) \;=\; -n\Delta\mu + \sigma A = -\frac{4\pi r_n^3}{3v_l} kT \ln S + \sigma 4\pi r_n^2$$



Für den kritischen Radius:

$$\left.\frac{\partial \Delta G}{\partial r}\right|_{r_n = r_n^*} = 0$$

$$r_n^* = \frac{2\sigma v_l}{kT \ln S}$$

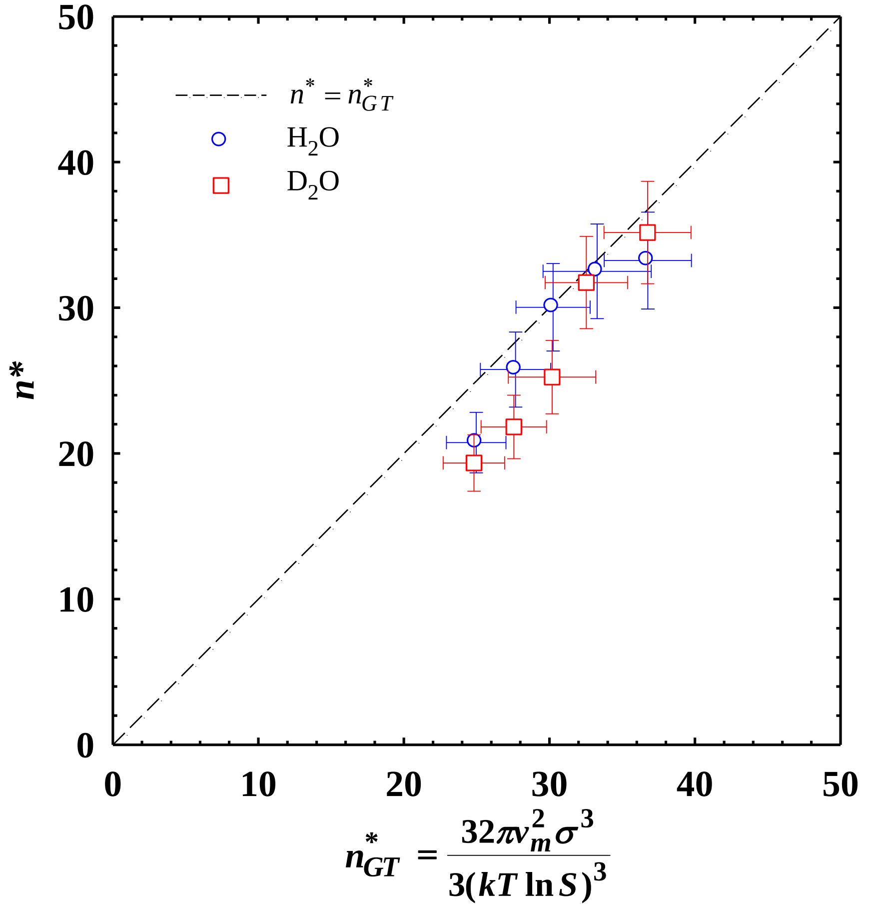
kritische Clustergröße

Test der *Gibbs-Thomson* Gleichung

$$r_n^* = \frac{2\sigma v_l}{kT \ln S}$$

$$n = \frac{4\pi r^3}{3 v_l}$$

$$n_{GT}^* = \frac{32\pi v_l^2 \sigma^3}{3\left(kT \ln S\right)^3}$$



D. Kashchiev, J. Chem. Phys. 76, 5098 (1982)

Theorie - CNT

$$\Delta G(n) \;=\; -n\Delta\mu + \sigma A = -\frac{4\pi r_n^3}{3v_l} kT \ln S + \sigma 4\pi r_n^2$$

$$r_n^* = \frac{2\sigma v_l}{kT \ln S} \qquad\qquad \Delta G^* = \frac{16\pi v_l^2 \sigma^3}{3\left(kT \ln S\right)^2}$$

$$J_{CNT} = K \exp\left(\frac{-\Delta G^*}{kT}\right) = K \exp\left(\frac{-16\pi v_l^2 \sigma^3}{3\left(kT\right)^3 \left(\ln S\right)^2}\right)$$

Theorie

- **Classical nucleation theory [Becker and Döring 1935]:**

$$J_{CNT} = \sqrt{\frac{2\sigma}{\pi m}} v_l \left(\frac{p_v}{kT} \right)^2 \exp\left\{ -\frac{16\pi v_l^2 \sigma^3}{3(kT)^3 (\ln S)^2} \right\}$$

- **Self consistent theory [Girshick and Chiu 1990]:**

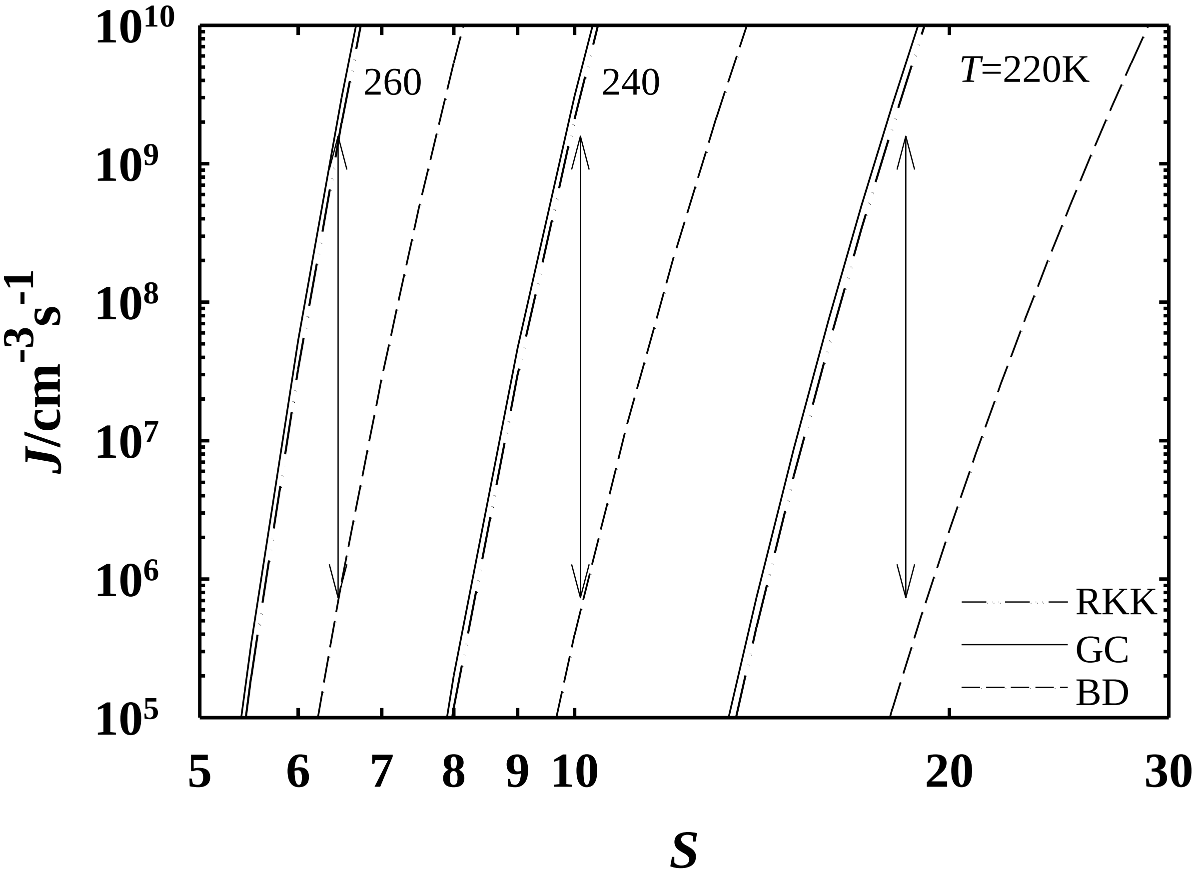
$$\Delta G_{GC} = -(n-1)\Delta\mu + \sigma A_n - \Theta \quad \Theta = \frac{(36\pi)^{1/3} v_l^{2/3} \sigma}{kT} \quad J_{GC} = J_{CNT} \frac{1}{S} \exp(\Theta)$$

- **Reiss-Kegel-Katz theory [Reiss, Kegel and Katz 1997]:**

$$J_{RKK} = \frac{R_e}{S} J_{BD} = \frac{1}{S} \sqrt{\frac{v_l}{kT\kappa n}} \exp\{\Theta\} J_{CNT} = \sqrt{\frac{v_l}{kT\kappa n}} J_{GC}$$

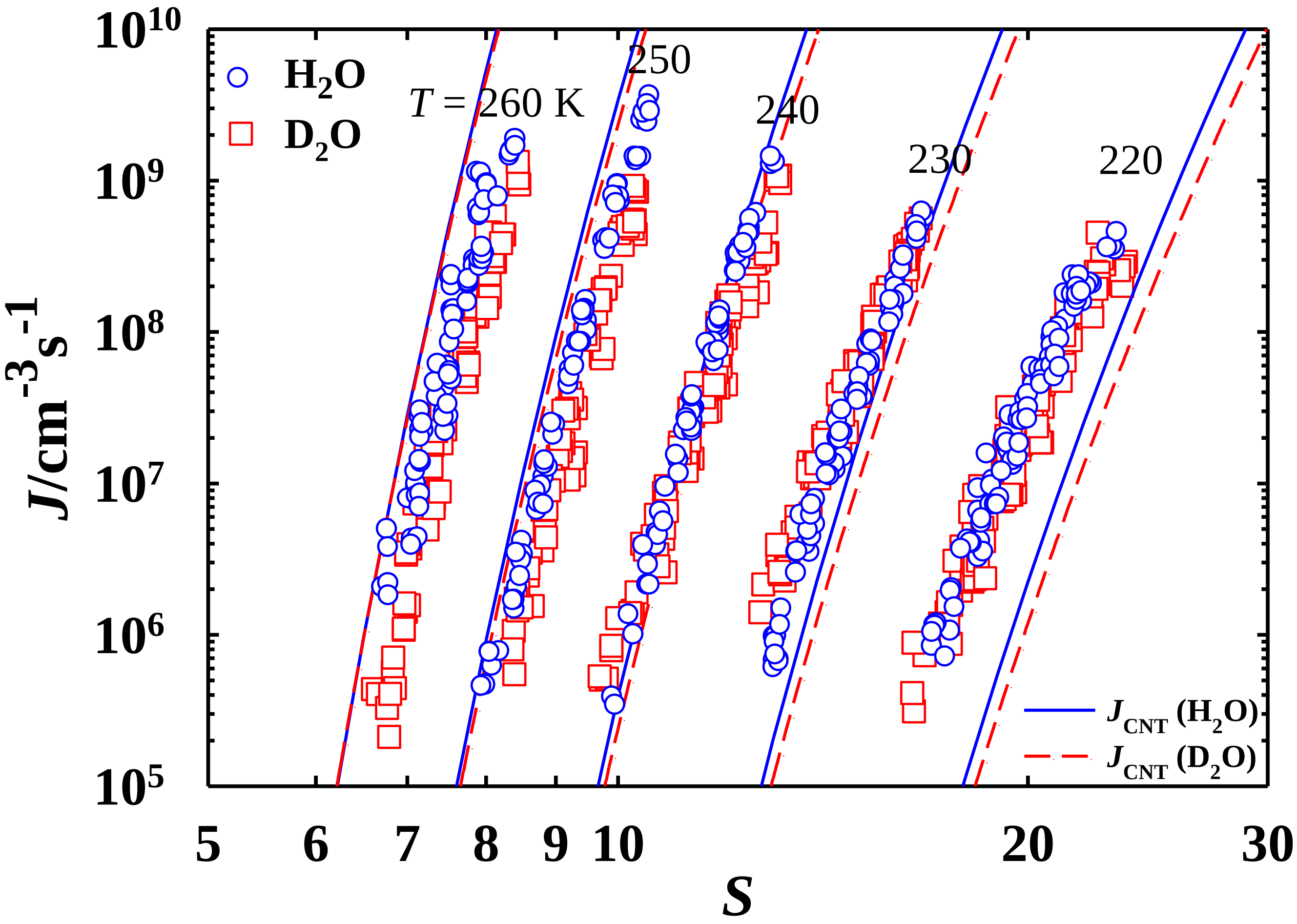
R. Becker und W. Döring, Ann. Phys., **24**, 719 (1935**)**
S.L.Girshick and C.P. Chiu, J. Cherm. Phys. **93**,1273 (1990)
H.Reiss, W.K.Kegel,, J.L:Katz, Phys.Rev.Lett., **78**, 4506 (1997)

Theorie



10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
J/cm^{-3}s^{-1}
5
6
7
8
9
10
20
30
S
260
240
T=220K
RKK
GC
BD

Keimbildungsraten / Wasser



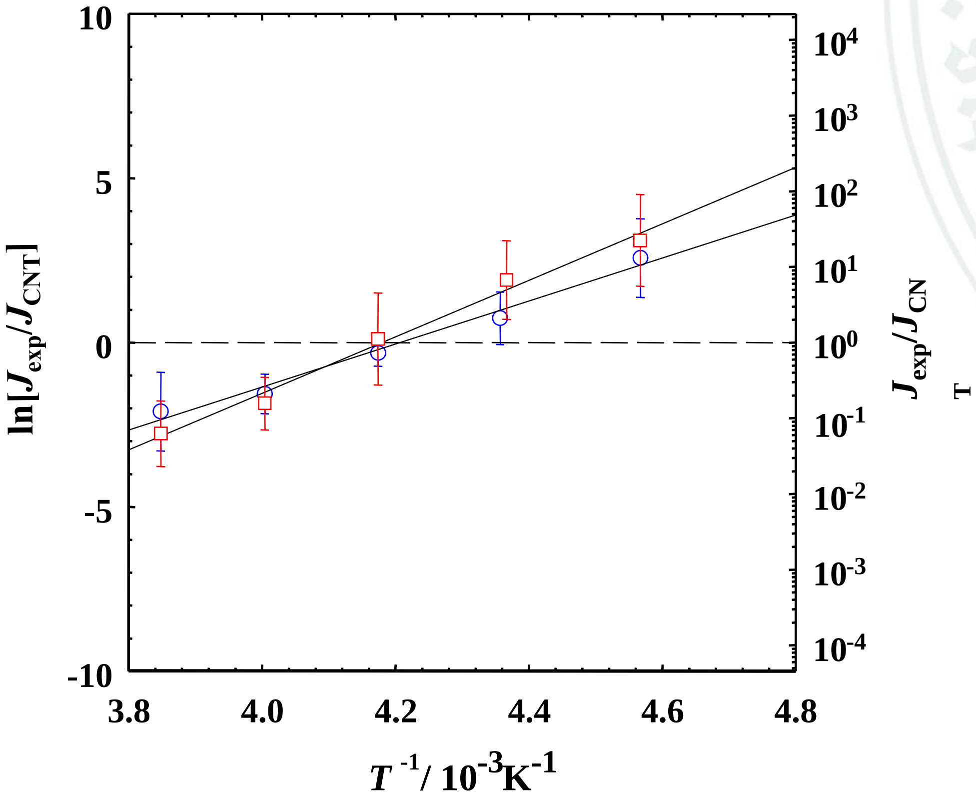
J. Wölk and R. Strey, J. Phys. Chem. B, 105, 11683 (2001)

Analyse

Theorie: $J_{\mathrm{CNT}} = K_{\mathrm{CNT}} \exp(-\Delta G^{*}_{\mathrm{CNT}} / kT)$

Experiment: $J_{\mathrm{exp}} = K_{\mathrm{exp}} \exp(-\Delta G^{*}_{\mathrm{exp}} / kT)$

$$\ln \frac{J_{\mathrm{exp}}}{J_{\mathrm{CNT}}} = \ln \frac{K_{\mathrm{exp}}}{K_{\mathrm{CNT}}} + \frac{\Delta G^{*}_{\mathrm{CNT}} - \Delta G^{*}_{\mathrm{exp}}}{kT}$$



$$\ln \frac{J_{\mathrm{exp}}}{J_{\mathrm{CNT}}} = A + B\frac{1}{T}$$

○ **H_2O:**

$A = -27.56$

$B = 6.5 \cdot 10^{3}\,\mathrm{K}$

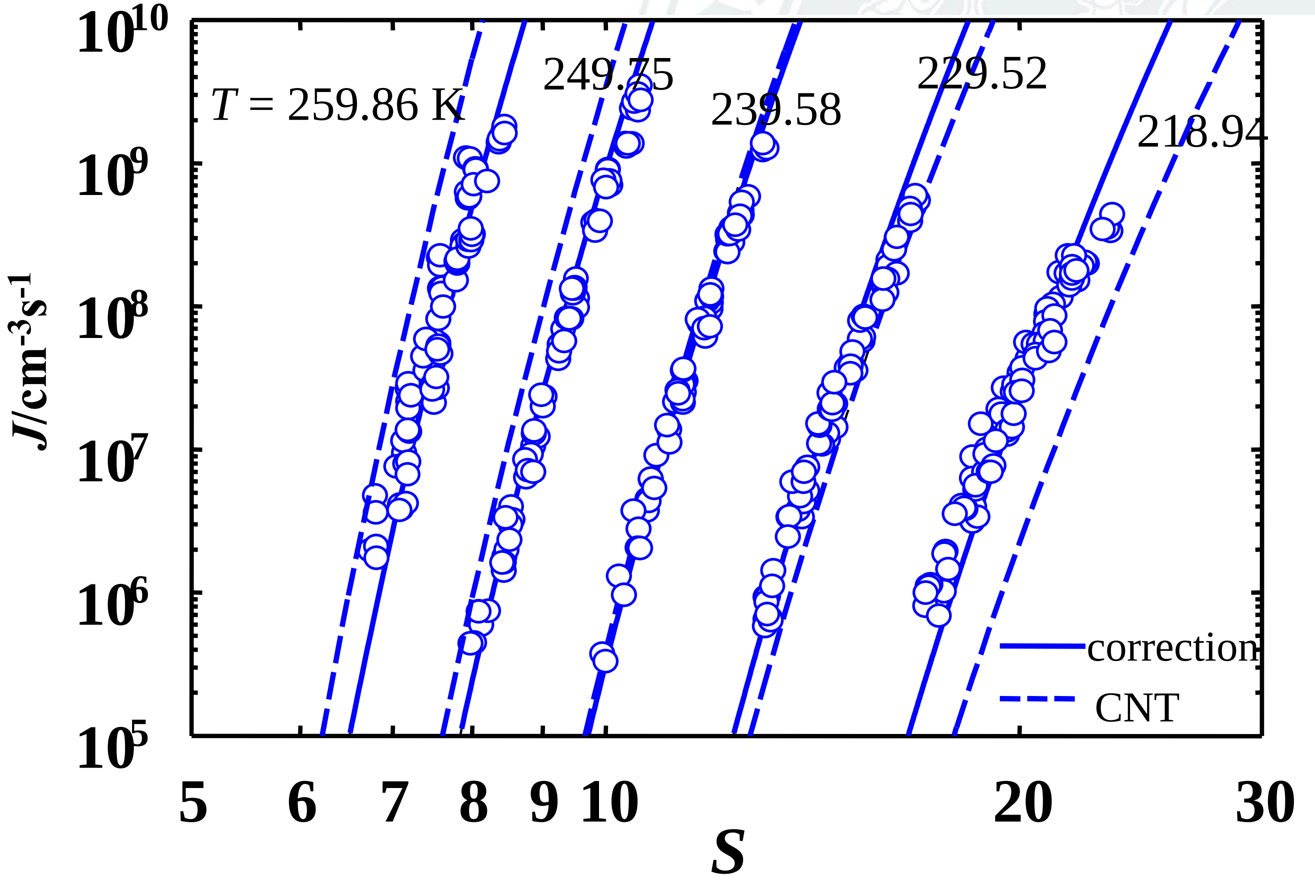
□ **D_2O:**

$A = -35.98$

$B = 8.6 \cdot 10^{3}\,\mathrm{K}$

J. Wölk and R. Strey, J. Phys. Chem. B, 105, 11683 (2001)

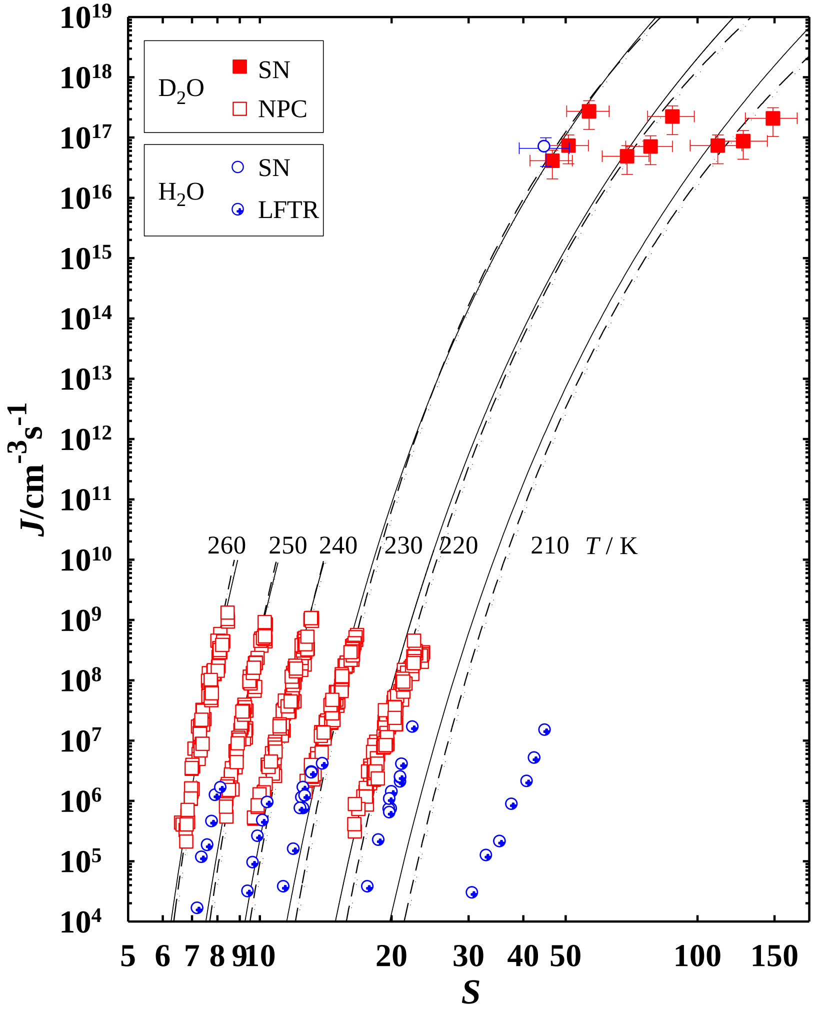
empirische Korrelation



J. Wölk, R.Strey, C.H. Heath and B.E. Wyslouzil, J. Chem. Phys. 117, 4954 (2002)

Keimbildungsraten

—— J_{corr}



Mikheev, V.B.; Irving, P.M.; Laulainen, N.S.; Barlow, S.E.; Pervukhin, V.V. J. Chem. Phys. 116, 10772 (2002)

J. Wölk and R. Strey, J. Phys. Chem. B, 105, 11683 (2001)

Kim Y.J. Wyslouzil B.E. Wilemski G. Wölk J. Strey R. J. Phys. Chem. A 108, 4365 (2004)