

How ambient pressure influences water droplet nucleation at tropospheric conditions

Antti-Pekka Hyvärinen,¹ David Brus,^{1,2} Jan Wedekind,³ and Heikki Lihavainen¹

Received 6 August 2010; revised 8 September 2010; accepted 21 September 2010; published 3 November 2010.

[1] Nucleation theories typically neglect the influence of the ambient pressure on the condensation of droplets from a supersaturated vapor, despite increasing experimental evidence. We have applied a recently presented model that incorporates this effect to the homogeneous nucleation rates of water at tropospheric conditions. We measured experimental pressure dependent nucleation rates of water in helium at low to intermediate pressures (70–200 kPa) and at temperatures from 240–270 K with the laminar flow diffusion chamber. The observed pressure effect shows a clear positive effect (increasing nucleation rate with increasing pressure) at 270 K and a weaker effect with lower temperatures, consistent with the theory. The experimental pressure effect was more pronounced than predicted by theory. The same principle of the pressure effect should also hold for heterogeneous nucleation of water, which implies that water vapor removal by droplet nucleation of water may be suppressed at tropospheric conditions. **Citation:** Hyvärinen, A.-P., D. Brus, J. Wedekind, and H. Lihavainen (2010), How ambient pressure influences water droplet nucleation at tropospheric conditions, *Geophys. Res. Lett.*, 37, L21802, doi:10.1029/2010GL045013.

1. Introduction

[2] Homogeneous and heterogeneous nucleation of water vapor in the atmosphere plays a key role in formation of both liquid and ice phase clouds. Water vapor itself is an important greenhouse gas. Understanding its nucleating behavior is thus of great importance, because the formation of ice clouds is a major mechanism removing the water vapor from air entering the stratosphere [e.g., *Holton and Gettleman*, 2001]. Yet, contradicting observations of atmospheric water vapor have been made in recent years, challenging the principles of current understanding of ice cloud formation and water distribution in the upper troposphere [e.g., *Peter et al.*, 2006].

[3] Understanding homogeneous vapor to liquid nucleation forms the backbone of investigating the more complex nucleation processes, as the same principles can often be applied in all these cases. One such effect is the influence of the total pressure on the nucleation rate. It was generally assumed that the presence of a non-condensable carrier gas

does not influence the clustering process. However, experiments since the 1980s have brought forth quite ambiguous results on the influence of the amount and the type of the carrier gas on the observed nucleation rate. A comprehensive review of the subject is given by *Brus et al.* [2006], and, as noted by *Anisimov et al.* [2009], the pressure effect is deemed as one of the most challenging topics in nucleation research. The measurements conducted by *Brus et al.* [2006, 2008] and *Hyvärinen et al.* [2006] in diffusion based devices increased the knowledge of the carrier gas effect on *n*-alcohols. Concurrently, *Wedekind et al.* [2008] presented a simple model that explains the pressure effect by a competition of two contributions: non-isothermal effects and pressure-volume work, from here on denoted as the “full pressure effect” theory. The theoretical predictions presented in the paper agreed well with the corresponding MD (Molecular Dynamics) simulations of Lennard–Jones argon. *Hyvärinen et al.* [2009] compared experimental pressure dependent nucleation rates of different *n*-alcohols and nucleation rates obtained from the “full pressure effect” theory. A good agreement was found between theory and experiment for *n*-pentanol + helium and *n*-butanol + helium systems.

[4] We now apply these techniques to assess the pressure effect in an atmospherically relevant case: homogeneous nucleation of water. We have measured pressure dependent nucleation rates of water in helium and compared these results with the “full pressure effect” theory. Our findings corroborate the trends predicted by the “full pressure effect” theory and indicate that the removal of water through droplet nucleation may be suppressed considerably under tropospheric conditions.

2. Methods

[5] The experimental studies were carried out at the Finnish Meteorological Institute, Helsinki, in a laminar flow diffusion chamber (LFDC). The detailed experimental setup, design, operation principle and validation of proper operation for pressure –related measurements were discussed in details by *Brus et al.* [2008] and *Hyvärinen et al.* [2006]; and for water-related measurements by *Manka et al.* [2010]. In the previous papers, different error sources were considered: uncertainties in the transport properties (namely equilibrium vapor pressure, binary diffusion coefficient, and thermal conductivity of the mixture), non-ideal behavior of the vapor-carrier gas mixture, effect of total pressure on surface tension, and shortcomings of the mathematical model used to calculate the flow profiles in the LFDC. None of these were able to explain the observed pressure effect. The total pressure in the experiments conducted here varied between 70–200 kPa. Helium was used as a carrier gas, as air was not suitable due to heat- and mass transfer limitations in the flow tube

¹Finnish Meteorological Institute, Helsinki, Finland.

²Laboratory of Aerosol Chemistry and Physics, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Prague, Czech Republic.

³Departament de Física Fonamental, Universitat de Barcelona, Barcelona, Spain.

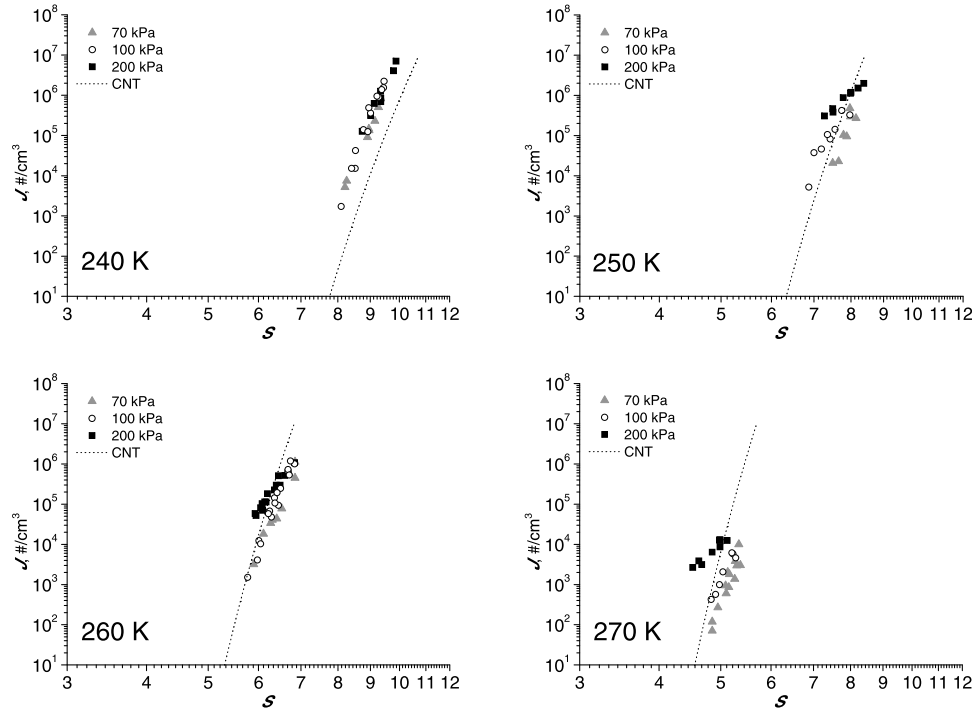


Figure 1. Isothermal nucleation rates, J as a function of saturation ratio, S of water in helium measured at three different total pressures. CNT denotes to Classical Nucleation Theory.

experiments with water. From theoretical point of view (see equations (1)–(6)), this should not affect the pressure effect considerably.

[6] The “full pressure effect” theory considers the efficiency of thermalization and the additional work that a cluster has to do against the ambient pressure. First presented by *Feder et al.* [1966], the prior is controlled by the competition between the energy increase due to latent heat and the energy removal through elastic collisions with vapor and carrier-gas molecules. Assuming for ideal gas behavior,

$$J_{nonisoth} = \frac{b^2}{b^2 + q^2} J_{isoth} \quad (1)$$

Here, the parameters q and b^2 are

$$q = h - \frac{k_B T}{2} - \gamma \frac{\partial A(n)}{\partial n} \quad (2)$$

and

$$b^2 = 2k_B^2 T^2 \left(1 + \frac{N_c}{N} \sqrt{\frac{m}{m_c}} \right). \quad (3)$$

Parameter q quantifies the energy released when a monomer is added to a cluster, where h is the latent heat per molecule (obtained from the Clausius-Clapeyron equation), k_B is the Boltzmann constant, T is temperature, γ is surface tension and A is the surface area $= s_1 n^{2/3}$, $s_1 = (36\pi v_1^2)^{1/3}$, v_1 is the volume occupied by a liquid molecule. Parameter b^2 is the mean squared energy fluctuation removed by collisions, where N is the number of molecules, m is the molecular mass, and subscript c denotes the carrier gas.

[7] The additional work that a cluster has to do against the pressure of the carrier gas is cast in the nucleation rate

expression of the classical nucleation theory (CNT) by modifying the free energy barrier ΔG_{pV}^* with the pressure of the carrier gas through a change of the chemical potential $\Delta \mu_{eff}^2$, resulting in modified nucleation rate J_{pV} :

$$J_{pV} = K \exp\left(-\frac{\Delta G_{pV}^*}{k_B T}\right) \quad (4)$$

$$\text{where } \Delta G_{pV}^* = (16\pi/3) \left(v_l^2 \gamma^3 / \Delta \mu_{eff}^2 \right) \quad (5)$$

$$\text{and } \Delta \mu_{eff}^2 = k_B T \ln S - v_l (p + p_c - p_{eq}) \quad (6)$$

The modified chemical potential arises naturally from the proper integration of the Gibbs-Duhem equation [*Wedekind et al.*, 2008]. Here, K is the kinetic prefactor, S is the saturation ratio, p and p_{eq} are the partial- and equilibrium vapour pressures of the condensable, respectively, and p_c is the carrier gas pressure. Finally, the “full pressure effect” of the carrier gas on the nucleation rate J_{PE} becomes

$$J_{PE} = \frac{b^2}{b^2 + q^2} J_{pV}. \quad (7)$$

It is worth pointing out that non-ideality of the vapor and carrier-gas can also be included easily, provided that sufficiently accurate equations of state are available.

3. Results

[8] The experimental nucleation rate isotherms were measured at 240–270 K with three different total pressures of 70, 100 and 200 kPa. The low pressure of 70 kPa corresponds to

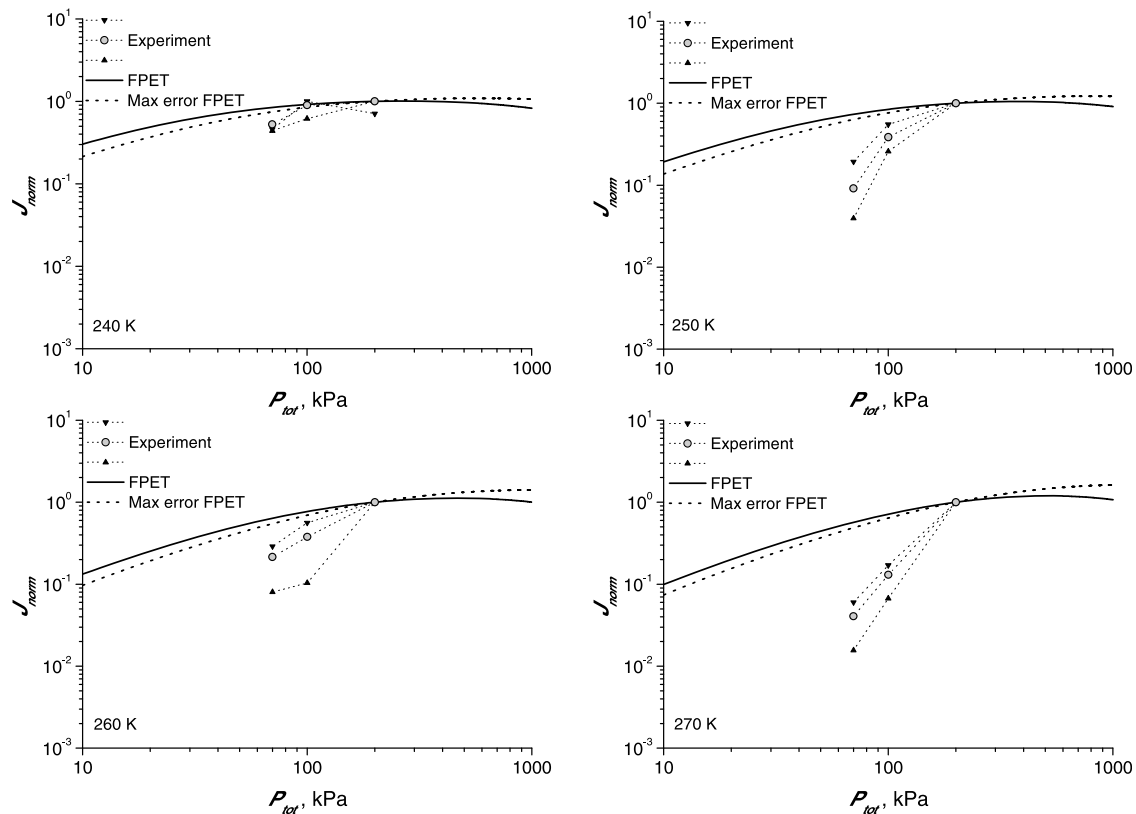


Figure 2. Normalized nucleation rate J_{norm} , as a function of total pressure P_{tot} . Circles are experimental values taken at the median saturation ratio of each isotherm, and downward and upward triangles are experimental values at the highest and lowest measured saturation ratio, respectively. FPET denotes to “full pressure effect theory” calculated at the median saturation ratio of each isotherm, equation (7), and “Max error estimate” denotes sensitivity analysis for the theory, see text for details.

an altitude of about 3000 m in the atmosphere and represents tropospheric conditions. The pressure range was limited by the technique used to count the nucleated and grown particles (an adopted optical head of the CPC TSI 3010), and the stability of the instrument. The measured data are presented in Figure 1 and compared against the Classical Nucleation Theory (CNT) [Becker and Döring, 1935]. The tabulated data can be found as Table S1 of the auxiliary material.¹ These data are a continuation to that measured by Manka *et al.* [2010] at atmospheric pressure with the same LFDC and the 100 kPa results fall to the same line within the error limits.

[9] It can be seen that at 270 K there is a clear positive pressure effect (increasing nucleation rate with increasing pressure). Isotherms 250 and 260 K show a weak positive effect which is somewhat hidden in the experimental scatter of the data. At 240 K there is no pressure effect at the prevailing measurement conditions. It is notable that the slopes of the isotherms at 70 kPa and 100 kPa are steeper than those measured at 200 kPa. We cannot explain this feature at this time, but the same observation was made with measurements of *n*-butanol and *n*-pentanol [Brus *et al.*, 2008; Hyvärinen *et al.*, 2006]. In addition, the 200 kPa slopes vary somewhat between the different isotherms. We assume this to be a measurement inaccuracy related to the

instability of the instrument with icing of the LFDC walls. Due to icing, the instrument cannot be run in a typical steady state for more than 0.5–3 min [see Manka *et al.*, 2010]. This would increase the problems when pushing the instrument towards its limits, i.e., when measuring at untypically high or low pressures.

[10] To compare the experimental results with the theoretical prediction of the “full pressure effect” (equation (7)), we plotted the normalized nucleation rates as a function of total pressure (Figure 2). For the normalization, we first made linear fit of $d \ln J / d \ln S$ to the experimental data for each temperature and total pressure. The experimental maximum rate at the pressure it appeared was set to unity; and the nucleation rates at the other pressures and at the same saturation ratio were scaled with this. This was done at the median saturation ratio for each isotherm, and the highest and lowest saturation ratio covered by all three pressure levels. Theoretical values (calculated at the saturation ratio for the experimental median value for each isotherm) were normalized separately, with the value at 200 kPa set to unity. It can be assumed that the pressure effect deducted at the medians of saturation ratios for each isotherm would represent the data best, as these points are measured in the middle of the operational boundaries. It can be seen that the theory corresponds to the experiments rather well. It explains the positive effect observed at 270 K and practically no-effect observed at 240 K.

¹Auxiliary materials are available in the HTML. doi:10.1029/2010GL045013.

[11] The biggest difference between the predicted and measured nucleation rate appears at the low pressure regime, where the measured nucleation rates exhibit a steeper rise with increasing pressure than predicted by theory. The same has been observed previously when comparing the nucleation rates of *n*-alcohols with the “full pressure effect” theory [Hyvärinen *et al.*, 2009]. This implies that in reality the thermalization at low pressures is even more inefficient than predicted by theory, or that other factors such as inaccuracy in surface tension come into play. We tested the sensitivity of the “full pressure effect” theory by changing all of the input parameters (except universal constants) in equations (2)–(6) by $\pm 10\%$. Figure 2 illustrates that even the cumulative effect of changing all the parameters in the direction to match the experimental results does not explain the difference. Yet, this is hardly surprising considering that the full pressure effect theory is based on CNT, which is notorious to large deviations. Nevertheless, both the non-isothermal effects and the pressure-volume work can—and should be included in improved theories of nucleation [Wedekind *et al.*, 2008], which could provide a promising route towards more accurate quantitative predictions.

4. Conclusions

[12] We presented the first experimental pressure-dependent nucleation rates of water in helium at low to intermediate pressures (70–200 kPa). The “full pressure effect” theory is able to catch the correct pressure dependent nucleation rates of water. In our measuring window, the influence of the pressure is primarily determined by the non-isothermal correction, first presented by Feder *et al.* [1966]. This is because the measurements were conducted in a pressure range where the negative pressure effect caused by the pV -work plays little role. However, in an earlier study, the “full pressure effect” theory was found to predict also the negative effect [Hyvärinen *et al.*, 2009]. The “full pressure effect” theory fails to predict the steep rise seen in the experimental nucleation rates at low pressures as a function of increasing pressure. This implies that the thermalization at low pressures is even more inefficient than predicted by theory. However, it should be pointed out that in condensation measurements of water conducted by Winkler *et al.* [2006], thermal accommodation coefficient was determined to be unity even at 20 kPa total pressure.

[13] Our results suggest that lowering the pressure (comparable to increasing in altitude) suppresses nucleation, which is most prominent at mid-tropospheric conditions ($p_{tot} < 70$ kPa, 250 K $< T < 270$ K). However, the pressure effect is highly dependent on temperature, which somewhat cancels the effect when going up to upper troposphere and lower stratosphere. It should also be noted that the pressure effect was more pronounced for experiment compared to theory, so the theoretical estimations should be taken as the

lower estimate of the effect. Homogeneous vapor to liquid nucleation of water occurs very rarely in the atmosphere. However, the pressure effect principles are also directly applicable to heterogeneous nucleation, because the Fletcher theory [Fletcher, 1958] can be appended in a similar manner with non-isothermal contribution and the pressure-volume work. The Fletcher theory has just recently been found to give an accurate description of heterogeneous nucleation experiments performed by Winkler *et al.* [2008]. In the future, this prospect should be studied in more detail.

[14] **Acknowledgments.** The financial support by the Academy of Finland Centre of Excellence program (project 1118615) and of the KONE foundation are greatly acknowledged. We would like to thank David Reguera for his relentless support and guidance.

References

- Anisimov, M., *et al.* (2009), Vapor–gas/liquid nucleation experiments: A review of the challenges, *J. Aerosol Sci.*, *40*(9), 733–746, doi:10.1016/j.jaerosci.2009.06.002.
- Becker, D., and W. Döring (1935), Kinetische Behandlung der Keimbildung in übersättigten Dämpfen, *Ann. Phys.*, *416*(8), 719–752, doi:10.1002/andp.19354160806.
- Brus, D., *et al.* (2006), Homogeneous nucleation rate measurements of 1-propanol in helium: The effect of carrier gas pressure, *J. Chem. Phys.*, *124*, 164306, doi:10.1063/1.2185634.
- Brus, D., *et al.* (2008), The homogeneous nucleation of 1-pentanol in a laminar flow diffusion chamber: The effect of pressure and kind of carrier gas, *J. Chem. Phys.*, *128*, 134312, doi:10.1063/1.2901049.
- Feder, J., *et al.* (1966), Homogeneous nucleation and growth of droplets in vapours, *Adv. Phys.*, *15*, 111–178, doi:10.1080/00018736600101264.
- Fletcher, N. H. (1958), Size effect in heterogeneous nucleation, *J. Chem. Phys.*, *29*(3), 572–576, doi:10.1063/1.1744540.
- Holton, J. P., and A. Gettleman (2001), Horizontal transport and the dehydration of the stratosphere, *Geophys. Res. Lett.*, *28*(14), 2799–2802, doi:10.1029/2001GL013148.
- Hyvärinen, A.-P., *et al.* (2006), The carrier gas pressure effect in a laminar flow diffusion chamber: Homogeneous nucleation of *n*-butanol in helium, *J. Chem. Phys.*, *124*, 224304, doi:10.1063/1.2200341. (Correction, *J. Chem. Phys.*, *128*, 109901, doi:10.1063/1.2840353, 2008.)
- Hyvärinen, A.-P., *et al.* (2009), Carrier gas pressure effect in homogeneous nucleation of *n*-alcohols, in *Proceedings of the 18th International Conference on Nucleation and Atmospheric Aerosols 2009*, edited by J. Smolik and C. O’Dowd, pp. 642–645, Inst. of Chem. Process Fundam. ASCR, Prague.
- Manka, A., *et al.* (2010), Homogeneous water nucleation in a laminar flow diffusion chamber, *J. Chem. Phys.*, *132*(24), 244505, doi:10.1063/1.3427537.
- Peter, T., *et al.* (2006), When dry air is too humid, *Science*, *314*, 1399–1402, doi:10.1126/science.1135199.
- Wedekind, J., *et al.* (2008), Unravelling the “pressure effect” in nucleation, *Phys. Rev. Lett.*, *101*, 125703, doi:10.1103/PhysRevLett.101.125703.
- Winkler, P. M., *et al.* (2006), Condensation of water vapor: Experimental determination of mass and thermal accommodation coefficients, *J. Geophys. Res.*, *111*, D19202, doi:10.1029/2006JD007194.
- Winkler, P. M., *et al.* (2008), Heterogeneous nucleation experiments bridging the scale from molecular ion clusters to nanoparticles, *Science*, *319* (5868), 1374–1377, doi:10.1126/science.1149034.

D. Brus, A.-P. Hyvärinen, and H. Lihavainen, Finnish Meteorological Institute, Erik Palménin aukio 1, PO Box 503, FI-00101 Helsinki, Finland.
J. Wedekind, Departament de Física Fonamental, Universitat de Barcelona, Martí i Franquès 1, ES-08028 Barcelona, Spain.