On the effect of pressure and carrier gas on homogeneous water nucleation
M. A. L. J. Fransen, J. Hrubý, D. M. J. Smeulders, and M. E. H. van Dongen

Citation: The Journal of Chemical Physics 142, 164307 (2015); doi: 10.1063/1.4919249
View online: http://dx.doi.org/10.1063/1.4919249
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/142/16?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Prediction of the homogeneous droplet nucleation by the density gradient theory and PC-SAFT equation of state

The homogeneous nucleation of 1-pentanol in a laminar flow diffusion chamber: The effect of pressure and kind of carrier gas

Homogeneous nucleation at high supersaturation and heterogeneous nucleation on microscopic wettable particles: A hybrid thermodynamic/density-functional theory

Homogeneous nucleation rate measurements of 1-propanol in helium: The effect of carrier gas pressure

Homogeneous nucleation of droplets from a supersaturated vapor phase
On the effect of pressure and carrier gas on homogeneous water nucleation

M. A. L. J. Fransen,1,a) J. Hrubý,2 D. M. J. Smeulders,1 and M. E. H. van Dongen3
1Department of Mechanical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
2Institute of Thermomechanics, Academy of Sciences of the Czech Republic, Dolejškova 5, CZ-182 00 Prague 8, Czech Republic
3Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
(Received 9 March 2015; accepted 15 April 2015; published online 27 April 2015)

Homogeneous nucleation rates of water droplets were measured at a nucleation temperature close to 240 K in a Pulse-Expansion Wave Tube (PEWT). Several measures were taken to improve the data obtained with the PEWT. For instance, the molar water vapor fraction was determined with three independent techniques. The resulting standard uncertainty of the supersaturation was within 1.8%. Results are given for water nucleation in helium at 100 kPa and at 1000 kPa and in nitrogen at 1000 kPa. Two trends were observed: (i) the values of the nucleation rate of water in helium at 1000 kPa are slightly but significantly higher (factor 3) than its values at 100 kPa and (ii) nucleation rates of water in nitrogen at 1000 kPa are clearly higher (factor 10) than in helium at the same pressure. It is argued that the explanation of the two observed trends is different. For case (i), it is the insufficient thermalization of the growing water clusters in helium at the lowest pressure that has a reducing effect on the nucleation rate, although a full quantitative agreement has not yet been reached. For case (ii), thermal effects being negligible, it is the pressure dependency of the surface tension, much stronger for nitrogen than for helium, that explains the trends observed, although also here a full quantitative agreement has not yet been achieved. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4919249]

I. INTRODUCTION

Homogeneous condensation is the vapor-to-liquid phase transition in the absence of foreign particles. The first stage of condensation is the nucleation process, which is of paramount importance for meteorological models and climate studies.1 This subject has also much relevance for the petrochemical industry, in which water vapor is separated from natural gas.2 Many homogeneous water nucleation experiments were conducted in the past decades.3–7 With various experimental methods, the measured nucleation rates range from $10^4$ m$^{-3}$ s$^{-1}$ up to $10^{21}$ m$^{-3}$ s$^{-1}$. The nucleation pressures vary between 40 kPa and 4.0 MPa, while nucleation temperatures range from 200 K to 320 K.

Usually, the experimental data are compared with Classical Nucleation Theory (CNT).8,9 It is reported that the experimental nucleation rate dependency on both supersaturation10 and temperature7,10–13 consistently deviates from CNT predictions. Also for modified nucleation theories,14,15 satisfactory agreement with experimental data is still absent.16

Homogeneous nucleation experiments typically use a mixture of a vapor and a carrier gas. The role of this non-condensing carrier gas is to absorb the latent heat that is released by growing microscopic clusters. Brus et al.17 describe possible effects of pressure and carrier gas on nucleation. Few experimental studies exist for the case of water nucleation. Using an expansion tube, Barschdorff18 examined the effect of carrier gas for pure water vapor and water vapor mixed with several carrier gases such as helium, air, and argon. In the low pressure regime (∼5 kPa), he found that for identical initial conditions, the onset of condensation19 was dependent on carrier gas type. Pure water vapor expanded to a lower onset temperature than water mixed with a carrier gas. No systematic differences between the different carrier gases were found. Later, Viisanen et al.20 measured homogeneous nucleation rates with a nucleation pulse chamber21 in the atmospheric pressure range. For the carrier gases helium, neon, argon, krypton, and xenon, no significant differences in nucleation rate were observed. Wyslouzil et al.22 investigated the influence of pressure on the onset of condensation in a supersonic nozzle. In the atmospheric pressure range and at high nucleation rates typical for supersonic nozzles, no significant effect was found.

The only experimental study of water nucleation in the megapascal range was published by Luijten et al.23 who measured nucleation rates of water in helium and nitrogen. They found significant dependencies of the nucleation rate on pressure and carrier gas, which they ascribed to surface tension variations.

Hyvärinen et al.24 recently measured water nucleation rates in helium at low pressures (70 kPa–200 kPa) for temperatures between 240 K and 270 K. They found an increase in the nucleation rate, stronger than predicted by theory based on the work by Wedekind et al.,25 with increasing pressure at 270 K and a smaller increase at lower temperatures. Their explanation is that at lower pressure, the thermalization

---

a)Electronic mail: m.a.l.j.fransen@tue.nl
process—the collisions of the carrier gas molecules with the clusters which equilibrate temperature differences originating from release of latent heat of condensation—is less efficient than at high pressure. Feder et al.26 were the first to quantify this effect. Barrett et al.27,28 and Wedekind et al.25,29 slightly modified Feder’s work. In this paper, Barrett’s approach30 is used and experiments are carried out with a so-called Pulse-Expansion Wave Tube (PEWT).31,32

II. PURPOSE AND OUTLINE

The PEWT has been used extensively to investigate water nucleation.10,23,33–35 Luijten et al.23 performed the first comprehensive study at high pressure (1.0 MPa–4.0 MPa), and Holten et al.30 studied water nucleation in helium at atmospheric pressure (100 kPa). While systematic discrepancies between the two studies were found, it is the work by Holten et al. that shows excellent agreement with data by Wölk and Strey.12 In this paper, we present new experimental data and we take measures to eliminate the systematic discrepancies of the past (Sec. III). We studied the nucleation behavior of water for a temperature of 240 K in helium at 100 kPa and at 1000 kPa and of water in nitrogen at 1000 kPa. We will focus on two important effects that play a role in nucleation experiments: thermalization (Sec. III A) and the dependence of surface tension on pressure and carrier gas (Sec. III B). We reconsider the Langmuir adsorption model to estimate the importance of the surface tension change with pressure at the nucleation temperature. The results are presented in Sec. IV and the conclusions are presented in Sec. V.

III. EXPERIMENTS AND THEORY

The PEWT makes use of the nucleation pulse method,36 which separates the process of nucleation from that of droplet growth. The nucleation is confined to a short period of time Δt called the nucleation pulse, in which the pressure and temperature have fallen rapidly, and the supersaturation is high (10.5–15.5). The pulse duration is on the order of a millisecond and a cloud of clusters is formed. After the pulse, the pressure and temperature steeply rise, so that the nucleation process is quenched. Still, the supersaturation is larger than unity (6.5–8.5) to allow the clusters to grow to macroscopic sizes such that an almost monodispersed cloud of droplets is formed. The droplet cloud is investigated by means of different light scattering techniques.37 The nucleation rate J follows from J = n/Δt, where n is the droplet number density. The uncertainty of the nucleation rate is maximum 20% (on the order of the symbol size in the forthcoming plots), resulting mainly from the uncertainty of the pulse duration.

The supersaturation S is defined as38

\[ S = \frac{y p}{p_e}, \]

with y the molar water vapor fraction, p the total pressure, \( f(p, T) \) the enhancement factor, and \( p_e(T) \) the saturated vapor pressure; T denotes the temperature. The enhancement factor describes both the influence of total pressure on phase equilibrium (Poynting effect39,40) and of non-ideal gas behavior.

S = 1 corresponds with phase equilibrium. In the pressure range considered, helium can be regarded as an ideal gas without significant interaction with the vapor molecules. Then, for helium at a pressure of 1000 kPa, only a small Poynting effect contributes to the enhancement factor: f = 1.0093 (T = 240 K). For nitrogen at 1000 kPa, non-ideal gas behavior has to be incorporated and the enhancement factor f = 1.0539 (T = 240 K). The saturated vapor pressure correlation by Murphy and Koop41 was used. Holten42 compared this correlation with others43,44 and found no significant differences (<<1%) for a temperature of 240 K.

We improved the PEWT as follows:

1. The mixture preparation device,44 which produces the gas-vapor mixture with the desired molar water vapor fraction by means of two mass flow controllers, was equipped with an independent mass flow rate calibration device.
2. We have used recorded droplet growth curves to determine the supersaturation by post-processing. This was reported in an earlier publication.35
3. Two experimental techniques were added to determine the molar water vapor fraction: Chilled mirror hygrometry45 and Karl Fisher coulometry.46 The corresponding devices were installed in such a way that they could measure the gas-vapor composition of both the inflow and outflow of the PEWT. This is of importance because of possible water adsorption at the PEWT walls.
4. Next to the existing piezoelectric transducer (Kistler 603B), a piezoresistive pressure transducer (Kistler 4073) was installed (this was already implemented by Holten et al.10). The first has a better frequency response but only measures pressure changes, while the latter measures the absolute pressure values. By combining both readings, it is possible to determine the absolute pressure in the nucleation pulse with high accuracy (uncertainty <0.2%).
5. To determine the initial temperature, we use two independent thermometers (Tempcontrol PT-8316) with an accuracy of ±0.03 K.

Taking into account the uncertainty of the initial temperature, that of the initial and nucleation pressures, and that of the thermodynamic models,47 the uncertainty of the nucleation temperature was estimated (0.17 K). The molar water vapor fraction is measured threefold and its uncertainty is based on the most accurate method, i.e., the mixture preparation device. Consequently, the uncertainty of the water vapor fraction is also very low (within 1.0%). Using Eq. (1), we find a maximum uncertainty of the supersaturation of 1.8%.

A. Nonisothermal nucleation

Detailed theoretical thermalization studies were published previously.25–28,30,48,49 We use the nonisothermal model originally proposed by Feder et al.26 which was later modified by Barrett and co-workers.27,28 It describes the transitions in cluster size and cluster energy. This includes the release and attachment of vapor monomers by evaporation and condensation, as well as the increase and decrease of energy by latent heat release and (non-sticking) gas and vapor molecule
collisions with clusters.\textsuperscript{27} Using detailed balance in the two-dimensional (size and energy) space yields the evaporation rate.

Barrett\textsuperscript{30} derived the following approximate analytical solution for the nucleation rate (the same notation is used here):

\[
\frac{J}{J_{\text{iso}}} = \left[1 + \left(\frac{c_{\text{bv}} + H^2}{c_{\text{bv}}(1 + \lambda)}\right)\right]^{-1},
\]  

with \( J \) the nucleation rate, \( J_{\text{iso}} \) the isothermal nucleation rate which we aim to measure, and \( c_{\text{bv}} = c_{\text{bv}}/k \), with \( c_{\text{bv}} = c_v + k/2 \) the monomer heat capacity at constant volume, where \( k \) is the Boltzmann constant. The parameter \( H \) is given by

\[
H = \frac{mL}{kT} - \frac{1}{2} - \frac{c_v}{c_m} + \frac{2}{3(i^*)^{1/3}} \frac{d\theta}{dT},
\]

where \( m \) is the monomer mass, \( L \) the latent heat of vaporization, \( i^* = (20/3 \ln S)^3 \) the critical cluster size with \( \theta = a_1 \sigma/kT \) the dimensionless variant of the surface tension \( \sigma \), and \( a_1 = (36\pi)^{1/3}(v_r)^{2/3} \) the monomer surface area with the monomer volume in bulk liquid \( v_r \). The parameter \( H \) is expressed in terms of the classical model for the cluster (capillarity approximation), but is rather insensitive to the exact droplet model.\textsuperscript{28} The parameter \( \lambda \) is given by

\[
\lambda = \frac{c_{\text{bg}} n_i \bar{V}_g}{c_{\text{bg}} m \bar{V}},
\]

with \( c_{\text{bg}} = c_s + k/2 \) the heat capacity of the gas at constant volume, \( n_i \) the gas number density, \( \bar{V}_g \) the mean gas molecular speed, \( n_i \) the monomer number density in the vapor, and \( \bar{V} \) the mean molecular speed for vapor monomers. The parameter \( \lambda \) takes the influence of the carrier gas into account: \( \lambda = 0 \), if no carrier gas is present (nonisothermal situation), while \( \lambda \to \infty \) in the (ideal) isothermal case. The parameter \( \lambda \) is proportional to the ratio of the mean gas molecular speed \( \bar{V}_g \) and the mean molecular speed for vapor monomers \( \bar{V} \). This ratio is equal to the root of the molecular masses of the water vapor and the carrier gas. Hence, \( \lambda \) and, therefore, nonisothermal effects depend upon the molecular mass of the carrier gas.

Some assumptions in this nonisothermal nucleation model are disputable. For example, the condensation rate is not valid for very small clusters, because the assumption of a spherical shape (capillarity approximation) no longer holds. The sticking probability is assumed constant and taken equal to unity, whereas it is likely to be smaller than one and must decrease with decreasing cluster size and supersaturation.\textsuperscript{30}

\section*{B. Pressure dependency of the surface tension of water}

The reduction of the surface tension of water by carrier gas is thermodynamically related to the adsorption of gas molecules onto the liquid surface.\textsuperscript{31} Helium adsorsbs very little and, consequently, its effect on the surface tension is very weak in the relevant pressure and temperature ranges.\textsuperscript{32-54} For nitrogen, the influence on the surface tension of water can hardly be detected at atmospheric pressure, but becomes stronger at higher pressures.\textsuperscript{32-55} Unfortunately, no data exist in the supercooled liquid region. Luijten \emph{et al.}\textsuperscript{38} attempted to estimate the surface tension change with nitrogen pressure based on statistical mechanics. However, as shown in Fig. 1, the model largely underpredicted the effect of nitrogen pressure at elevated temperatures.\textsuperscript{52-55} For this reason, we reconsidered the Langmuir adsorption isotherm\textsuperscript{38,56}

\[
\sigma(p_g) = \sigma_0 - \frac{kT}{A_g} \ln \left(\frac{p_g + p_k}{p_k}\right),
\]

where \( \sigma(p_g) \) is the surface tension at the partial nitrogen gas pressure \( p_g \), which is assumed equal to the total pressure \( p \), \( \sigma_0 \) is the surface tension of pure water at saturated vapor pressure, \( A_g \) is the average surface area per adsorption site, and \( p_k \) is the Langmuir pressure. For the site adsorption area, we adopted an estimate by McClellan and Harnsberger\textsuperscript{57} who have reported a value of \( A_g = 1.6 \times 10^{-19} \text{ m}^2 \). This estimate is in reasonable agreement with other literature values.\textsuperscript{58} Although \( A_g \) can be treated as a constant, the Langmuir pressure is a strong function of temperature which can be given as

\[
p_k = \frac{kT}{v^A} \exp\left(\frac{u^A_g}{kT}\right).
\]

Here, \( v^A \) is the effective volume available for translation of an adsorbed molecule and \( u^A_g \) is the potential energy of the interaction of gas molecules with the liquid surface. The elementary derivation of Eq. (5) based on statistical thermodynamic arguments is given in the Appendix.

The values for parameters \( v^A \) and \( u^A_g \) were determined using several data sets for the dependency of the surface tension on nitrogen pressure at various temperatures.\textsuperscript{52-55} From these data sets, we determined the initial slopes of the surface tension vs. gas pressure plots at various temperatures

\[
\sigma_{\text{po}} = \lim_{p_g \to 0} \left(\frac{d\sigma}{dp_g}\right)_T = -\frac{kT}{A_g} p_k,
\]

where the pressure \( p \) in this limit case is equal to the saturated vapor pressure \( p_v \). The left-hand side of Eq. (7) can be obtained from experiments and can be compared with its right-hand side obtained from Eq. (6). When taking the logarithm and substituting the Langmuir pressure (Eq. (6)), we end up with
The logarithm of $\sigma_{\phi_0}$ as a function of the reciprocal temperature. The confidence bounds (dotted lines) show the 68% confidence intervals, which are based on the two error bars (solid circles). The linear fit (dash dotted line) results in the following parameter values: $v^A = 7.6 \times 10^{-30}$ m$^3$ and $u^A_g = -1.1 \times 10^{-20}$ J.

Figure 2 shows $\sigma_{\phi_0}$ as a function of the reciprocal temperature for all data points. The results of the various studies show considerable scatter. Therefore, mean values (solid circles) with error bars have been calculated at two temperatures (300 K and 375 K). These error bars show the standard uncertainties. The fitting process revealed the following values: $v^A = 7.6 \times 10^{-30}$ m$^3$ and $u^A_g = -1.1 \times 10^{-20}$ J. At 240 K and 1000 kPa nitrogen pressure, the estimated effect of pressure on the surface tension of water is a reduction by 1.5% ± 0.5%.

Recently, new accurate measurements of the surface tension of pure water under supercooled conditions at atmospheric pressure were published. It was proven experimentally that the extrapolated IAPWS (International Association for the Properties of Water and Steam) correlation adequately describes the surface tension of supercooled water. No indication of a second inflection point in the supercooled liquid region was found. For 240 K, we took the following value for the reference surface tension: $\sigma_0 = 79.95 \times 10^{-3}$ N m$^{-1}$.

IV. RESULTS AND DISCUSSION

Homogeneous water nucleation experiments were performed at a temperature of 240 K for different pressures and carrier gases. The data are available in electronic form as supplementary material. Results obtained with helium at a pressure of 100 kPa are shown in Fig. 3. Minute temperature-deviations that result from a slightly varying initial temperature were compensated using established post-processing. Our results are compared with experimental results by Holten et al., Hyvärinen et al., Manka et al., Wölk and Strey, and Miller et al. The data by Hyvärinen et al. and Manka et al. have been obtained with a laminar flow diffusion chamber that was used by both groups. Wölk and Strey, using a nucleation pulse chamber, and Miller et al., employing an expansion cloud chamber, used argon as carrier gas. Our data agree with results by Holten et al. that were also obtained with the PEWT and clearly coincide with the data by Wölk and Strey, thus proving the reliability of the PEWT at atmospheric pressure.

Next, we varied the carrier gas and its pressure. Figure 4 shows the results obtained for the following three cases: 100 kPa helium, 1000 kPa helium, and 1000 kPa nitrogen. The 100 kPa helium data are given for reference. We now discuss our results. Observation 1: the nucleation rate in helium is a factor of 3 higher when going from 100 kPa to 1000 kPa.
Observation 2: the nucleation rate is a factor of 10 higher when changing the carrier gas from helium to nitrogen at 1000 kPa. It is worth mentioning here that the present PEWT 1000 kPa results for both helium and nitrogen at 240 K are shifted over the $S$-axis by 15\% approximately with respect to the results previously reported by Luijten et al.\textsuperscript{33} This systematic change, already noted for helium by Holten et al.\textsuperscript{10} is attributed to an incorrect measurement of the supersaturation, temperature, or both by Luijten et al.\textsuperscript{33} With all the newly introduced measures to guarantee the highest quality (Sec. III) and the confirmation of the data by Holten et al.,\textsuperscript{10} we argue that the present results are reliable.

We note that a result similar to our first observation—an increase in nucleation rate when increasing the carrier gas pressure—was found by Hyvärinen et al.,\textsuperscript{24} albeit at low pressures (70 kPa–200 kPa) and higher temperature (270 K). Our second observation—an increase in nucleation rate when changing the carrier gas from helium to nitrogen—quantitatively substantiates earlier work by Luijten et al.\textsuperscript{33} To the best of our knowledge, these authors were the first to report on this carrier gas effect at high pressure.

The following explanations are proposed. Observation 1: we recognize an insufficient thermalization at 100 kPa helium pressure, which reduces the nucleation rate. At 1000 kPa, the nucleation process is fully isothermal, so insufficient thermalization is not an issue here. Using Eq. (2), we estimate the nonisothermal effect for our conditions ($p = 107$ kPa, $T = 240$ K, $S = 13$, and other physical properties taken from Ref. 35). We find that according to the theory of Barrett,\textsuperscript{30} the nucleation rate for our nonisothermal conditions is a factor 1.4 smaller than for isothermal conditions. In the experiments, we found a factor 3 increase in the nucleation rate when going from 100 kPa to 1000 kPa helium pressure (Fig. 4), so theory understimates the effect. The experimental increase in the nucleation rate as a function of pressure reported by Hyvärinen et al.\textsuperscript{24} was also more pronounced than theoretically predicted.

Observation 2: Thermal effects being negligible, we recognize the pressure dependency of the surface tension of water in nitrogen. To evaluate the resulting effect on the nucleation rate, we use the CNT,\textsuperscript{8,9}

$$J = K \exp\left[-\frac{4}{27} \frac{\theta^3}{(\ln S)^2}\right],$$

with the kinetic prefactor $K$. A small change in the surface tension results in

$$\frac{J}{J_0} = \exp\left[-\frac{4}{9} \frac{\theta^3}{(\ln S)^2} \frac{\Delta \theta}{\theta_0}\right],$$

where $J_0$ and $\theta_0$ are the reference nucleation rate and dimensionless surface tension and $\Delta \theta/\theta_0 = \Delta \sigma/\sigma_0 = -0.015 \pm 0.005$, we find a value between 2.7 and 7.4 for $J/J_0$. The increase of the nucleation rate of water droplets in nitrogen with respect to helium can therefore at least partly be explained by a decrease of the surface tension due to the nitrogen pressure.

In the framework of CNT, we assign macroscopic bulk values to parameters (such as the liquid density and surface tension) describing the microscopic cluster. This capillarity approximation is obviously not valid for our clusters with typical critical cluster sizes on the order of 20–30 molecules. A sophisticated nucleation theory describing the microscopic clusters in a more realistic way and improved modeling of the adsorption process on the molecular scale is therefore likely to lead to better agreement between experiment and theory.

V. CONCLUSION

The PEWT experimental facility was improved substantially in order to decrease the uncertainties in the measurements. This was achieved by adding two techniques to independently measure the molar water vapor fraction. This leads to an improvement of the maximum standard uncertainty in the supersaturation (within 1.8\%). Two cases were experimentally investigated at 240 K: (i) the influence of thermalization on nucleation using pressure variations and (ii) the dependence of surface tension on pressure at the nucleation temperature by varying carrier gases. A small but significant increase in nucleation rates (factor 3) was found when going from 100 to 1000 kPa helium pressure. The existing thermalization theory by Barrett\textsuperscript{30} (based on earlier work by Feder et al.\textsuperscript{26}), yielding an increase of a factor 1.4, predicts the correct trend qualitatively, similarly as was found by Hyvärinen et al.\textsuperscript{24} It was already noted by Hyvärinen et al.\textsuperscript{24} that the lack of quantitative agreement between experiment and theory is not fully surprising since the CNT itself is not accurately describing the nucleation process.

A significant increase (factor 10) in nucleation rates was measured when using nitrogen instead of helium at high pressure, which quantitatively substantiates earlier work by Luijten et al.\textsuperscript{33} We reconsidered the Langmuir adsorption isotherm and used existing experimental data at higher temperatures to assign values to the potential energy of the interaction of gas molecules with the liquid water surface and the effective volume available for translation of an adsorbed molecule. Helium adsorbs very little, but nitrogen does have an effect on the surface tension of water. The established model allowed us to estimate the dependency of the surface tension of water on nitrogen pressure. The reduction in surface tension at 240 K with 1000 kPa nitrogen pressure $1.5\% \pm 0.5\%$ at least partly explains the nucleation rate increase when using nitrogen instead of helium at a pressure of 1000 kPa, although, also here, a full quantitative agreement has not yet been achieved.

ACKNOWLEDGMENTS

The authors thank the technicians of the Department of Mechanical Engineering of the Eindhoven University of Technology for their help. J.H. gratefully acknowledges a support by Project No. P101-11-1593 of the Czech Science Foundation.

APPENDIX: DERIVATION OF THE LANGMUIR ADSORPTION ISOTHERM

We assume that the liquid surface has $K$ adsorption sites formed by suitable configurations of water molecules.
Certain part \( N_g^A \) of \( K \) adsorption sites is occupied by adsorbed gas molecules, where the superscript “A” refers to adsorbed gas molecules. Multiple occupation of the adsorption sites is not considered. Considering mutual indistinguishability of the adsorbed molecules, the number of configurations of the adsorbed layer is given by the binomial coefficient

\[
C = \frac{K!}{(K - N_g^A)!N_g^A!}.
\]  

(A1)

Equilibrium between the adsorbed gas molecules and the free gas molecules means that the chemical potentials must be the same

\[
\mu_A^g = \mu_g^G,
\]  

(A2)

where the superscript “G” refers to the free gas molecules. To find the chemical potentials, we first need to estimate their respective Helmholtz free energies. For the adsorbed case, it is given by

\[
F^A = U^A - TS^A.
\]  

(A3)

The internal energy \( U^A \) consists of contributions by internal molecular degrees of freedom \( u_g^{\text{int}} \), translation, and potential energy \( u_g^A \) of the interaction between the adsorbed gas molecules and the liquid surface,

\[
U^A = N_g^A(u_g^{\text{int}} + \frac{3}{2} kT + u_g^A).
\]  

(A4)

The potential energy of the interaction between the adsorbed gas molecules is neglected, because it is much weaker than the interaction between the gas molecules and the liquid surface for the systems studied. The entropy of the adsorbate can be estimated by

\[
S^A = N_g^A[s_g^{\text{int}} + k \ln \left( \frac{V_{\text{ref}}}{V} \right)] + S_c,
\]  

(A5)

where \( s_g^{\text{int}} \) is the internal molecular entropy, \( V_{\text{ref}} \) and \( V^A \) are, respectively, a reference volume and the effective volume available for translation of an adsorbed molecule. The configurational entropy \( S_c \) on a per molecule basis is given by

\[
S_c = -k \sum_i p_i \ln p_i,
\]  

(A6)

where \( p_i \) is the probability of a configuration. Since all the configurations of the adsorbed layer are considered as equally probable, the probability is simply the inverse of the number of configurations, i.e., \( p_i = 1/C \). We can therefore rewrite the configurational entropy using Eq. (A1) as

\[
S_c = -k \left[ \frac{1}{p_i} \ln p_i \right] = k \ln C.
\]  

(A7)

After introduction of the surface coverage \( \theta = N_g^A/K \) and applying Stirling’s approximation \( \ln x! \approx x \ln x - x \), we can rewrite Eq. (A7) into

\[
S_c = -k \left[ (1 - \theta) \ln(1 - \theta) + \theta \ln \theta \right].
\]  

(A8)

The chemical potential for the adsorbed case \( \mu_A^g \) can be found by investigating the differential \( dF^A \), which consists of three contributions,

\[
dF^A = -S^A dT + \sigma_g dA + \mu_A^g dN_g^A,
\]  

(A9)

with \( \sigma_g \) the contribution of the adsorbate to the surface tension and \( A \) the surface area. The general Gibbs adsorption equation is given by Ref. 8

\[
S dT + A d\sigma + \sum N_i d\mu_i = 0.
\]  

(A10)

The change of the surface tension due to variation of the chemical potential of the gas at constant temperature and chemical potential of the vapor is given by

\[
\sigma_g \approx -\frac{N_g^A}{A g} d\mu_g,
\]  

(A11)

where we have used \( A = A_g K \) with \( A_g \) the average surface area per adsorption site. Using the ideal gas law (and the constraints of constant temperature and chemical potential of the vapor), the differential of the chemical potential of the gas is given by

\[
d\mu_g = v_g dp = kT \frac{dp}{p}.
\]  

(A12)

Combining Eqs. (A11) and (A12) leads to

\[
\sigma_g = -\frac{\theta kT dp}{A_g p},
\]  

(A13)

To derive the expression for the surface coverage \( \theta \), we employ the equilibrium condition (Eq. (A2)). The chemical potential for the adsorbed gas molecules using Eqs. (A3)–(A5) is given by

\[
\mu_A^g = \frac{\partial F^A}{\partial N_g^A} = u_g^{\text{int}} + \frac{3}{2} kT + u_g^A
\]

\[-T s_g^{\text{int}} - kT \left( \frac{v^A}{V_{\text{ref}}} \right) - T \left( \frac{\partial S_c}{\partial N_g^A} \right)_{T,A}.
\]  

(A14)

The last partial derivative can be found using Eq. (A8),

\[
\left( \frac{\partial S_c}{\partial N_g^A} \right)_{T,A} = \left( \frac{\partial S_c}{\partial \theta} \right) \left( \frac{\partial \theta}{\partial N_g^A} \right)_{T,A} = \frac{1}{K} ( \frac{\partial S_c}{\partial \theta} ) = k \left[ \ln \left( \frac{1}{\theta} \right) \right].
\]  

(A15)

Using this result in Eq. (A14), we obtain the following expression for the chemical potential of the adsorbed gas molecules:

\[
\mu_A^g = u_g^{\text{int}} + \frac{3}{2} kT + u_g^A - T s_g^{\text{int}}
\]

\[-kT \left( \frac{v^A}{V_{\text{ref}}} \right) - kT \ln \left( \frac{1}{\theta} - 1 \right).
\]  

(A16)

The chemical potential for the gas phase \( \mu_g^G \) can be derived in a similar way. If the ideal gas law in the form \( v = N_g^G kT/p_g \) is used, we get the following simplified equation:

\[
\mu_g^G = u_g^{\text{int}} + \frac{3}{2} kT - T s_g^{\text{int}} + kT \ln \left( \frac{p_g V_{\text{ref}}}{kT} \right).
\]  

(A17)

Using Eqs. (A16) and (A17), we can write the equilibrium condition (Eq. (A2)) as

\[
u_A - kT \ln \left( \frac{v^A}{V_{\text{ref}}} \right) - kT \ln \left( \frac{1}{\theta} - 1 \right) = kT \ln \left( \frac{p_g V_{\text{ref}}}{kT} \right).
\]  

(A18)
Straightforward algebra leads to a new expression for the surface coverage,

$$\theta = \left(1 + \frac{p_L}{p_g}\right)^{-1}, \quad (A19)$$

where we introduced the Langmuir pressure (Eq. (6))

$$p_L = \frac{kT}{v} \exp\left(\frac{\mu_g^L}{kT}\right).$$

The integration of Eq. (A13) using the surface coverage \(\theta\) of Eq. (A19) leads to the following surface tension (Eq. (5)):

$$\sigma(p_g) = \sigma_0 - \frac{kT}{A_g} \ln\left(\frac{p_g + p_L}{p_L}\right),$$

where \(\sigma_0\) is the surface tension of the pure substance.

For small surface coverages, i.e., \(\theta \ll 1\), we have

$$\theta \approx \frac{p_g}{p_L}, \quad (A20)$$

and integration of Eq. (A13) using Eq. (6) leads to an expression linear in gas pressure,

$$\sigma(p_g) = \sigma_0 - \frac{kT}{A_g} \exp\left(-\frac{\mu_g^L}{kT}\right) p_g = \sigma_0 + \sigma_0 p_g. \quad (A21)$$