PHYSICAL INTERPRETATION OF ICE CONTACT ANGLES, FITTED TO EXPERIMENTAL DATA ON IMMERSION FREEZING OF KAOLINITE PARTICLES


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Previous cloud chamber experiments on freezing of supercooled cloud droplets with single immersed, size-selected 400 nm and 800 nm kaolinite particles revealed a sigmoidal increase of the fraction of frozen cloud droplets with decreasing temperature in the range from 243 to 236 K. Assuming uniformity of the particle composition and horizontal homogeneity of the phase compatibility, applying classical nucleation theory (CNT), and fitting the microscopic “ice contact angle” to these experimental freezing probabilities disclosed a negative temperature coefficient of the ice contact angle, revealing an apparent increase of the cryophobia of the freezing catalyst. On the basis of Derjaguin’s thermomechanic concept of the disjoining pressure, a conceptual model is proposed that links the semi-empirical ice contact angle to its generating molecular interaction forces by extrapolating macroscopic relations to microscopic scales. Within the framework of a closure study with consideration of a comprehensive set of physical constraints for the water/ice/kaolinite system, this model is used to determine the residual molecular interaction force, which is necessary to reproduce the experimentally derived ice contact angles. The residual interaction force is on the order of magnitude of steric oscillation forces at the kaolinite/ice interfacial layer and corresponds to a temperature-dependent negative line tension of \(-5\text{ to }-28\) pN. The line tension behavior is discussed in the light of previous findings on heterogeneous water nucleation on solid surfaces and computer simulations of the water/ice/kaolinite system. Uncertainties originating from the employed model assumptions, especially interference due to interparticle variability are analyzed. Finally, observational requirements for a conclusive discrimination between inter- and intraparticle effects are discussed.

KEY WORDS: nucleation, contact angles, disjoining pressure, line tensions

1. INTRODUCTION

The improvement of cloud and rain prediction in atmospheric models depends, among others, on a better understanding and description of cloud freezing processes, affecting microphysical (including electrical, mechanical, thermal, aerodynamic, rheological, and surface) properties of hydrometeors (e.g., Fletcher, 1966; Hobbs, 1974; Khvorostyanov and Curry, 2014; Pruppacher and Klett, 1997; Sedunov, 1974); and their optical properties (e.g., Kokhanovsky, 2006;
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>dimensionless scaling parameter for type B interaction in Eq. (20)</td>
</tr>
<tr>
<td>( a_0, a_1, a_2 )</td>
<td>regression parameters in Eq. (1)</td>
</tr>
<tr>
<td>( a_R )</td>
<td>regression parameter</td>
</tr>
<tr>
<td>( a_s, a_b )</td>
<td>ion activity near the surface (outer Helmholtz plane) and in the bulk of the solution</td>
</tr>
<tr>
<td>( A )</td>
<td>cross section of the embryo of radius ( R )</td>
</tr>
<tr>
<td>( A_c )</td>
<td>contact area enclosed by the contact line between phases ( \alpha, \beta, ) and ( \gamma )</td>
</tr>
<tr>
<td>( A_{(\beta\gamma)}, \tilde{A}_{(\beta\gamma)} )</td>
<td>apparent (visible) and microphysically rough (actual) contact areas between the phases ( \beta ) and ( \gamma )</td>
</tr>
<tr>
<td>( A^H_{(\alpha\beta\gamma)} )</td>
<td>three-media (phases ( \alpha, \beta, ) and ( \gamma )) Hamaker constant</td>
</tr>
<tr>
<td>( b, B, C, D )</td>
<td>auxiliary variables</td>
</tr>
<tr>
<td>( c_{\text{OH}^-}, c_{\text{H}<em>3\text{O}^+}, c</em>{\ominus} )</td>
<td>molarities of hydroxid and hydronium ions and of a solute in an infinite-diluted solution</td>
</tr>
<tr>
<td>( D^{(\beta)} )</td>
<td>molecule diameter of a volume-equivalent sphere of phase ( \beta )</td>
</tr>
<tr>
<td>( e )</td>
<td>elementary (or electric) charge</td>
</tr>
<tr>
<td>( E_B )</td>
<td>molar Boltzmann energy</td>
</tr>
<tr>
<td>( E_{\text{ads}} )</td>
<td>molar and molecular adsorption energy</td>
</tr>
<tr>
<td>( \delta E_X )</td>
<td>residual molar energy</td>
</tr>
<tr>
<td>( f_{\text{I, stoch}}, f_{\text{I, pdf}} )</td>
<td>frozen droplet fraction (from stochastic and pdf model)</td>
</tr>
<tr>
<td>( f_{\text{II}}, f_{\text{II}}^{(A/B)} )</td>
<td>dimensionless dispatcher function (of type A and B interactions)</td>
</tr>
<tr>
<td>( F_\theta )</td>
<td>cumulative distribution function of the contact angle</td>
</tr>
<tr>
<td>( F_{\text{Grahame}}, F_{\text{Site}} )</td>
<td>governing functions for the net surface charge density satisfying electroneutrality of the electric double layer and a site-binding condition</td>
</tr>
<tr>
<td>( h_p )</td>
<td>Planck constant</td>
</tr>
<tr>
<td>( h_0 )</td>
<td>geometric length defined in Fig. 1</td>
</tr>
<tr>
<td>( \Delta h, \Delta h^{(*)} )</td>
<td>film thickness defined in Fig. 1 and effective film thickness</td>
</tr>
<tr>
<td>( I^{(\beta)} )</td>
<td>ionic strength of phase ( \beta )</td>
</tr>
<tr>
<td>( J_{\text{net}} )</td>
<td>heterogeneous nucleation rate</td>
</tr>
<tr>
<td>( K_{L}, K_{S} )</td>
<td>dimensionless line and surface roughness factors</td>
</tr>
<tr>
<td>( K_w )</td>
<td>dimensionless ionization constant of water at standard molality ( m^0 )</td>
</tr>
<tr>
<td>( K^{(1)}<em>{\chi^+/}, K^{(II)}</em>{\chi^+/} )</td>
<td>first- and second-order reaction rates of proton-acceptor [Eq. (A.6)] and proton-donor reactions [Eq. (A.10)] of placeholder X</td>
</tr>
<tr>
<td>( K'<em>{\chi^+/}, K'</em>{\chi^-} )</td>
<td>equilibrium constants of the proton-acceptor [Eq. (A.7)] and proton-donor reactions [Eq. (A.11)] of placeholder X</td>
</tr>
<tr>
<td>( K_{\chi^+}, K_{\chi^-} )</td>
<td>surface reaction or surface adsorption equilibrium constant for the proton-acceptor [Eq. (A.9)] and the proton-donor reactions [Eq. (A.12)] of placeholder X</td>
</tr>
<tr>
<td>( L )</td>
<td>half thickness of the QLL sandwiched between a charged and an electrically neutral surface</td>
</tr>
<tr>
<td>( L_d )</td>
<td>characteristic thickness of the electric double layer</td>
</tr>
<tr>
<td>( L_{M}, L_{S}, L_{V} )</td>
<td>molar enthalpies of ice melting, ice sublimation, and water vaporization</td>
</tr>
<tr>
<td>( L^{(\alpha\beta\gamma)}, \tilde{L}^{(\alpha\beta\gamma)} )</td>
<td>apparent (visible) and microphysically rough (actual) length of the contact line between phases ( \alpha, \beta, ) and ( \gamma )</td>
</tr>
</tbody>
</table>
### NOMENCLATURE (continued)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m^0$</td>
<td>standard molality</td>
</tr>
<tr>
<td>$m^{(\alpha\beta\gamma)}$</td>
<td>phase compatibility parameter at the contact line between phases $\alpha$, $\beta$, and $\gamma$</td>
</tr>
<tr>
<td>$m_{ij}^{(\alpha\beta\gamma)}$, $m_{ij}^{(\alpha\beta\gamma)}$</td>
<td>contributions to the phase compatibility parameter originating from interface energies and line tension</td>
</tr>
<tr>
<td>$M_w$</td>
<td>molar mass of water</td>
</tr>
<tr>
<td>$^{z_i}$</td>
<td>placeholder for an ion species with valency $z_i$ (cation or anion)</td>
</tr>
<tr>
<td>$n$</td>
<td>cluster aggregation number and auxiliary variable</td>
</tr>
<tr>
<td>$n_{\text{vis}}^{(\alpha)}$, $n_{\text{vis}}^{(\beta)}$, $n_{\text{vis}}^{(\gamma)}$</td>
<td>refractive indices of phases $\alpha$, $\beta$, and $\gamma$ in the visible range of the electromagnetic spectrum</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro constant</td>
</tr>
<tr>
<td>$N_{\text{Al}}$, $N_{\text{Si}}$</td>
<td>surface concentrations of amphoteric alumina and silica sites</td>
</tr>
<tr>
<td>$p$, $p_0$</td>
<td>pressure</td>
</tr>
<tr>
<td>$p_0$</td>
<td>probability density function of ice contact angle $\theta$</td>
</tr>
<tr>
<td>$r$</td>
<td>radius defined in Fig. 1</td>
</tr>
<tr>
<td>$R = R_{\text{crit}}$</td>
<td>radius of the critical embryo of phase $\alpha$ defined in Fig. 1</td>
</tr>
<tr>
<td>$R_{c}$</td>
<td>contact radius (radius of the contact area) defined in Fig. 1</td>
</tr>
<tr>
<td>$R_0$</td>
<td>offset radius (regression parameter)</td>
</tr>
<tr>
<td>$R_u$</td>
<td>universal gas constant</td>
</tr>
<tr>
<td>$R_N$</td>
<td>particle radius</td>
</tr>
<tr>
<td>$s^{(\alpha)}$, $s^{(\beta)}$</td>
<td>specific entropies of phases $\alpha$ and $\beta$</td>
</tr>
<tr>
<td>$S^{(\alpha\beta\gamma)}$</td>
<td>spreading coefficient of phase $\alpha$ at the contact line between phases $\alpha$, $\beta$, and $\gamma$</td>
</tr>
<tr>
<td>$S^{(\beta\gamma\delta)}$</td>
<td>spreading coefficient of phase $\beta$ at the contact line between phases $\beta$, $\gamma$, and $\delta$</td>
</tr>
<tr>
<td>$T$, $T_0$</td>
<td>temperature</td>
</tr>
<tr>
<td>$\theta^{(\alpha)}$</td>
<td>specific volume of hexagonal ice (phase $\alpha$)</td>
</tr>
<tr>
<td>$V_0$</td>
<td>geometric volume of the noncontact space</td>
</tr>
<tr>
<td>$V^{(\alpha)}$</td>
<td>volume of an elementary cell of hexagonal ice (phase $\alpha$)</td>
</tr>
<tr>
<td>$V_{\text{cell}}$</td>
<td>volume of the critical ice embryo of phase $\alpha$</td>
</tr>
<tr>
<td>$V_{\text{II}}, V_{\text{II}}^{(A/B)}$</td>
<td>effective volume of molecular interaction (of type A and B interactions)</td>
</tr>
<tr>
<td>$x$</td>
<td>auxiliary variable</td>
</tr>
<tr>
<td>$X$</td>
<td>placeholder for chemical elements Al, Si</td>
</tr>
<tr>
<td>$z$</td>
<td>geometric length defined in Fig. 1</td>
</tr>
<tr>
<td>$z_{\text{OH}^-}$, $z_{\text{H}_3\text{O}^+}$, $z_i$</td>
<td>valence of hydroxid ions, hydronium ions, and bulk-reservoir ions</td>
</tr>
</tbody>
</table>

### Greek Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_D(x)$</td>
<td>Dirac delta function of argument $x$</td>
</tr>
<tr>
<td>$\delta_T$</td>
<td>Tolman length</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>minimum spacing between phases $\alpha$ and $\gamma$ in the contact region, defined in Fig. 1 (characteristic length scale of type A interactions)</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>dielectric constant of the vacuum</td>
</tr>
<tr>
<td>$\epsilon_{\alpha}$, $\epsilon_{\beta}$, $\epsilon_{\gamma}$</td>
<td>static dielectric constants of phases $\alpha$, $\beta$, and $\gamma$</td>
</tr>
<tr>
<td>$\epsilon_{\alpha}^{(\alpha)}$, $\epsilon_{\alpha}^{(\beta)}$, $\epsilon_{\alpha}^{(\gamma)}$</td>
<td>relative dielectric constants of phases $\alpha$, $\beta$, and $\gamma$</td>
</tr>
<tr>
<td>$\epsilon_0^{(\beta)}$, $\epsilon_0^{(\gamma)}$</td>
<td>bulk value of $\epsilon^{(\beta)}$</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>electrostatic potential at the outer Helmholtz plane</td>
</tr>
<tr>
<td>$\eta$</td>
<td>auxiliary variable (parameter constant)</td>
</tr>
</tbody>
</table>
**NOMENCLATURE (continued)**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ, θ(αβγ)</td>
<td>contact angle at the contact line between phases α, β, and γ (ice contact angle)</td>
</tr>
<tr>
<td>̄θ, θ₀</td>
<td>arithmetic mean and modal value of the contact angle</td>
</tr>
<tr>
<td>̃θ, θ₀</td>
<td>contact angle at the contact line between phases α, β, and γ (ice contact angle)</td>
</tr>
<tr>
<td>κ(αβγ)</td>
<td>line tension of the contact line between phases α, β, and γ</td>
</tr>
<tr>
<td>κ₇, κ₀</td>
<td>regression coefficients (for function σ(αβ)/T)</td>
</tr>
<tr>
<td>λ, λ₀</td>
<td>effective and_dispatcher length scales of molecular interaction</td>
</tr>
<tr>
<td>̃λ</td>
<td>electromagnetic wavelength</td>
</tr>
<tr>
<td>Λ</td>
<td>characteristic length scale of molecular interaction</td>
</tr>
<tr>
<td>Λᵰ, Λ′ᵰ</td>
<td>Debye length scale and its twice value</td>
</tr>
<tr>
<td>Λₜ</td>
<td>characteristic length scale of dielectric interaction</td>
</tr>
<tr>
<td>μ</td>
<td>free parameter in the probability density function of the contact angle (mean value of the natural logarithm of the contact angle)</td>
</tr>
<tr>
<td>νₑ</td>
<td>main electronic absorption frequency in the ultraviolet (UV)</td>
</tr>
<tr>
<td>ξ</td>
<td>auxiliary variable (integration variable: geometric length, contact angle)</td>
</tr>
<tr>
<td>Π, Π₀</td>
<td>disjoining pressure and characteristic value of the disjoining pressure</td>
</tr>
<tr>
<td>δΠ₀ₓ</td>
<td>residual value of the characteristic disjoining pressure</td>
</tr>
<tr>
<td>ρ(α), ρ(β), ρ₁,∞(br)</td>
<td>molar densities of phases α and β, and of bulk-reservoir ions</td>
</tr>
<tr>
<td>ρ(α)</td>
<td>mass density of hexagonal ice (phase α)</td>
</tr>
<tr>
<td>σ(αβ), σ(αβ)</td>
<td>interface energy at the α/β interface and its bulk value</td>
</tr>
<tr>
<td>σ⁺(αγ)</td>
<td>interface energy at the α/γ interface</td>
</tr>
<tr>
<td>σ⁺(βγ), σ⁺(γδ)</td>
<td>interface energy at the β/γ and γ/δ interfaces</td>
</tr>
<tr>
<td>σ₀</td>
<td>net surface charge density</td>
</tr>
<tr>
<td>σ₁</td>
<td>charge density at the outer Helmholtz layer (OHP)</td>
</tr>
<tr>
<td>σᵣ</td>
<td>charge density at the inner Helmholtz layer (IHP)</td>
</tr>
<tr>
<td>σₛ</td>
<td>charge density at the solid surface</td>
</tr>
<tr>
<td>∆σ⁺(αβ)</td>
<td>corrective value of σ⁺(αβ)</td>
</tr>
<tr>
<td>∆σ⁺(βγ)</td>
<td>corrective value of σ⁺(βγ)</td>
</tr>
<tr>
<td>∆σ⁺(γδ)</td>
<td>corrective value of σ⁺(γδ)</td>
</tr>
<tr>
<td>σ⁺(δθ)</td>
<td>interface energy at the δ/θ interface</td>
</tr>
<tr>
<td>σ⁺(γδ)</td>
<td>interface energy at the γ/δ interface</td>
</tr>
<tr>
<td>Τᵣᵣᵣ</td>
<td>induction or residence time of particles in the cloud chamber</td>
</tr>
<tr>
<td>Φᵣᵣᵣⱼ</td>
<td>interaction potential in noncontact area (of type A and B interactions)</td>
</tr>
<tr>
<td>Ψᵣᵣᵣ=ζ, Ψᵣᵣᵣ=ξ</td>
<td>electrostatic potential at the outer Helmholtz layer (OHP) and inner Helmholtz layer (IHP)</td>
</tr>
<tr>
<td>Ψᵣᵣᵣₛ</td>
<td>electrostatic potential at the solid surface</td>
</tr>
<tr>
<td>Subscripts</td>
<td></td>
</tr>
<tr>
<td>EDF</td>
<td>electrodynamic forces</td>
</tr>
<tr>
<td>ESF</td>
<td>electrostatic forces</td>
</tr>
<tr>
<td>SOF</td>
<td>steric oscillation forces</td>
</tr>
<tr>
<td>X</td>
<td>annotation for residual term</td>
</tr>
</tbody>
</table>
Interpretation of Ice Contact Angles

Superscripts

\(\alpha\) embryonic phase (ice)

\(\beta\) maternal phase (supercooled water)

\(\gamma\) paternal phase (catalyzer)

\(\delta\) primordial phase (water vapor)

Hobbs, 1974; Liou, 1980; Lynch et al., 2002; Twomey, 1974, 1977a,b). Heterogeneous freezing of supercooled cloud droplets in Earth’s atmosphere plays an important role at temperatures higher than \(-38^\circ C\) (e.g., Hobbs, 1974; Pruppacher and Klett, 1997). It can be effectively described within the framework of classical nucleation theory (CNT) (e.g., Jeffery and Austin, 1997; Pruppacher and Klett, 1997; Khvorostyanov and Curry, 2000, 2004a,b, 2009, 2014) and is the only practical way to parametrize homogeneous and heterogeneous nucleation in atmospheric models (see, Hellmuth et al., 2013, for a review of CNT application to atmospheric freezing). In contrast to homogeneous freezing, heterogeneous freezing of supercooled water requires the presence of foreign bodies, called ice nuclei (IN), which are able to catalyze the formation of critical ice embryos. Mineral dust has been identified as an abundant species in the troposphere, which may act as efficient IN (Salam et al., 2006, see references therein).

The ability of foreign bodies to serve as freezing catalyzers for cloud water depends on both their physicochemical efficiency (quality) and their abundance (quantity) in the free troposphere. The particle abundance is controlled by source (e.g., dust mobilization) and sink (e.g., deposition) processes. The sink strength, in turn, is controlled by the dry particle deposition velocity, which is a function of the particle diameter. The deposition velocity of dry particles typically assumes its minimum in the diameter range of about 100–1000 nm (Seinfeld and Pandis, 1998, p. 970), which correlates well with the appearance of a broad mode in the typical aerosol number concentration in the free troposphere (Seinfeld and Pandis, 1998, p. 437, Fig. 7.19 therein), i.e., less deposition leads to higher atmospheric particle abundance. Therefore, the diameter range of 100–1000 nm is of preferential interest in the context of ice nucleation in supercooled clouds. Many details of the mechanism by which foreign bodies may act as IN are still obscure (e.g., Wex et al., 2014).

Experiments of Zobrist et al. (2007) on heterogeneous ice nucleation of supercooled water droplets coated with a nonadecanol monolayer, which served in this case as the catalyzing substrate, revealed a negative temperature coefficient of the contact angle \(\theta(\alpha\beta\gamma)\) at the contact line between a nucleated ice embryo (phase \(\alpha\)), supercooled water (phase \(\beta\)), and an alcohol film serving as the catalyzer (phase \(\gamma\)), i.e., \(d\theta(\alpha\beta\gamma)/dT < 0\) in the temperature range \(248 K \leq T \leq 268 K\). This behavior was qualitatively explained (i) by a gradual, temperature-dependent rearrangement of the 2D crystalline structure of Langmuir-like films formed by long-chain alcohols (carbon chains from C16 to C31), and (ii) by an increasing structural mismatch between the ice and organic film lattices as temperature decreases. According to the authors, \(\theta(\alpha\beta\gamma)\) scales with the temperature-dependent energy required for molecular rearrangement to enable a structural match between the ice embryo and the catalyzer. The negative temperature coefficient of the ice contact angle suggests a reduced flexibility of the alcohol monolayer to adapt to the ice structure (and an increased rearrangement energy) at lower temperature.

Welti et al. (2012) performed chamber studies on heterogeneous freezing of supercooled cloud droplets, which included single immersed, size-selected 400 nm and 800 nm kaolinite particles in the temperature range of \(T = 236–243 K\). Kaolinite is a bilayered aluminosilicate mineral and belongs to the most common minerals on Earth. It is mined as kaolin for many industrial purposes. Kaolinite clay is formed from chemical weathering of rocks in hot, moist climates. As kaolinite and montmorillonite are considered to be the main components of ice-nucleating tropospheric mineral dusts in the submicrometer range (Salam et al., 2006, see references therein), both minerals frequently serve as the \textit{Drosophila} of cloud freezing experiments, allowing intercomparability and process-oriented conditioning in cloud chamber setups. Typical diameters of size-selected kaolinite particles investigated in laboratory freezing experiments are, e.g., 300 nm in the study of Augustin-Bauditz et al. (2014), 300 and 700 nm in Wex et al. (2014), and 300, 700, and 1000 nm in Hartmann et al. (2016), covering the atmospherically relevant particle size
range. Applying CNT and assuming smoothness, uniformity, and equality of the surface for all kaolinite particles, Welti et al. (2012) derived the best fitting value of the angle $g^{(\alpha\beta\gamma)}$ at the contact line between a nucleated ice embryo (phase $\alpha$), supercooled water (phase $\beta$), and the catalyzing kaolinite particle (phase $\gamma$) by minimizing the mean square deviation between the experimentally measured and the calculated CNT-based frozen droplet fraction in the temperature interval $232 \, K \leq T \leq 246 \, K$. On the basis of the graphical data taken from the original paper, we have approximated the cosine of the contact angle by the following quadratic function of temperature [Welti et al., 2012, Eqs. (1)–(5), Figs. 4 and 9 therein]:

$$m^{(\alpha\beta\gamma)}(T) = \cos g^{(\alpha\beta\gamma)} = \frac{\sigma^{(\beta\gamma)} - \sigma^{(\alpha\gamma)}}{\sigma^{(\alpha\beta)}} \approx a_0 + a_1T + a_2T^2,$$

where $m^{(\alpha\beta\gamma)}$ denotes the fitted three-phases compatibility parameter\(^{+}\) with $\sigma^{(\alpha\beta)}$, $\sigma^{(\alpha\gamma)}$, and $\sigma^{(\beta\gamma)}$ denoting the interface energies at the ice/water, ice/substrate, and water/substrate interfaces, respectively. For the same nucleation system, Ickes et al. [2017, Eq. (8), Table 1, and scheme no. 7 therein] derived a linearly fitted function of $m^{(\alpha\beta\gamma)}(T)$, which agrees very well with Eq. (1). On the basis of the CNT calculus presented in Welti et al. [2012, Eq. (2) therein], the radius of the critical ice embryo in the temperature interval $232 \, K \leq T \leq 246 \, K$ can be approximated by a linear function of temperature in the form $R_{\text{crit}}(T) \approx a_0T + R_0$, with $a_0 = 5.71 \times 10^{-11} \, m \cdot K^{-1}$, $R_0 = -1.206 \times 10^{-8} \, m$, delivering $R_{\text{crit}}(242 \, K) \approx 1.77 \, nm$ and $R_{\text{crit}}(234 \, K) \approx 1.31 \, nm$. Equation (1) delivers $m^{(\alpha\beta\gamma)}(242 \, K) = 0.132$ (weak phase compatibility) and $m^{(\alpha\beta\gamma)}(234 \, K) = -0.364$ (moderate phase discompatibility), i.e., the phase compatibility apparently decreases upon increasing supercooking ($\left|\frac{dm^{(\alpha\beta\gamma)}}{dT}\right| > 0$ and $\frac{dm^{(\alpha\beta\gamma)}}{dT} < 0$). Welti et al. (2012) interpreted the negative temperature coefficient as an “evidence for an increase in the importance of the nucleation kinetics to ice formation as the temperature of homogeneous freezing is approached i.e., a decrease in the reduction of the Gibbs free energy for nucleation by the compatibility factor [...]. Surface features lowering the contact angle of an ice embryo to the substrate become increasingly important toward higher temperatures” (Welti et al., 2012, p. 9904). On the base of the Young equation and empirical values for $\sigma^{(\alpha\beta)}$ and $\sigma^{(\beta\gamma)}$ from the literature, those authors estimated $\sigma^{(\alpha\gamma)}(243 \, K) \approx 0.078 \, J \cdot m^{-2}$ and $\frac{d\sigma^{(\alpha\gamma)}}{dT} \approx -0.0013 \, J \cdot m^{-2} \cdot K^{-1}$, and concluded “that it is plausible to attribute a change in contact angle to change in surface tension with temperature. However, to conclude on the physical meaning of this finding, is out of scope of this study” (Welti et al., 2012, p. 9904).

It should be emphasized that the ice contact angle, derived as a fitting parameter from freezing experiments and given by Eq. (1), is not treatable as a “true” observable but just as a pseudo-observable, as (i) it eludes direct observation on the nanoscopy scale and (ii) its derivation relies on the theoretical details of the employed nucleation rate calculus. Despite this fact, the ice contact angle is a well-defined physical property, which reflects the phase compatibility of the ice/water/substrate system and is, at least under certain conditions, determinable from computer simulations. The observational indesiveness of $m^{(\alpha\beta\gamma)}(T)$ implies a certain degree of fuzziness in its physical interpretation and in the identification of the key determinants controlling the phase compatibility (and freezing capability). This applies especially to the impossibility to unambiguously distinguish between intra- and interparticle factors of influence. In view of this unpreventable uncertainty, we are unable to give a conclusive physical explanation of the observed phenomenon. Here, we will interprete the described phenomenon as an intraparticle phenomenon and address the following questions of interest: (i) Is the pseudo-observed ice contact angle reconcilable with available knowledge about water, ice, and kaolinite from empirical data, molecular theory, and computer simulations? (ii) Is our knowledge (in form of available thermo-, electro-, and optophysical and physicochemical data) sufficient to “close” an interface model presented here for the determination of the ice contact angle, and if not, what is the missing interaction link? In the present study, a physical interpretation of $\frac{d\omega^{(\alpha\beta\gamma)}}{dT} < 0$ for the water/ice/kaolinite system of Welti et al. (2012) will be given within the framework of a closure study on the base of the generalized Young equation with consideration of the theory of molecular interactions at interfaces and of a comprehensive set of physical constraints for the water/ice/kaolinite system.

\(^{+}\)The authors derived $m^{(\alpha\beta\gamma)}$ as a fitting parameter from their experiments but did not present their fitting function. Hence, Eq. (1) was rederived on the basis of the corresponding graph published in the cited paper.
2. DESCRIPTION OF THE CONTACT ANGLE MODEL

2.1 Model Assumptions

The contact angle model is based on the following assumptions:

- The population of IN is considered to consist of monodisperse particles of the same chemical composition with essentially the same physical parameters. The conditions of immersion freezing in one supercooled water droplet are considered to be representative for all other supercooled droplets of this population, and the interface model is assumed to be applicable for all droplets of the population. This means, that interparticle variability is precluded, and the temperature dependence of the contact angle is considered an intraparticle phenomenon.

- The system of interest comprises four phases: a supersaturated water vapor atmosphere (primordial phase $\delta$), a supercooled water droplet (maternal phase $\beta$), a nucleated ice germ (embryonic phase $\alpha$), and a catalyzing solid substrate (kaolinite, paternal phase $\gamma$), which is immersed in the supercooled water droplet.

- The substrate is assumed to have a flat surface with an infinitesimally small curvature and to be ideally smooth without any irregularities (kinks, cavities, protrusions, etc.). Thus, capillary forces originating from penetration of liquids in pores of rough media are neglected. The substrate surface is assumed to be completely wettable by water, allowing for the formation of a liquid droplet around the particle (e.g., Adamson and Gast, 1997; Brezesinski and Mögel, 1993; Kuni et al., 1996; Sonntag, 1977):

$$S(\beta\gamma\delta) = \sigma(\gamma\delta) - \left(\sigma(\beta\delta) + \sigma(\beta\gamma)\right) \geq 0,$$

where $S(\beta\gamma\delta)$ denotes the water spreading coefficient, $\sigma(\beta\delta)$, $\sigma(\gamma\delta)$, and $\sigma(\beta\gamma)$ are the liquid/vapor, substrate/vapor, and liquid/substrate interfacial energies, respectively.

- Upon supercooling of the liquid droplet containing the immersat (kaolinite), an ice embryo is formed by heterogeneous nucleation on the substrate surface. This ice embryo is assumed to be a segment of an ideal, rigid sphere with radius $R = R_{\text{crit}}(T)$, sessile on the flat substrate and forming the contact area $A_c = \pi R_c^2$, where $R_c$ denotes the contact radius. At the contact line formed by the intersection of the $\alpha\beta$, $\beta\gamma$, and $\alpha\gamma$ interfaces, the ice contact angle $\theta(\alpha\beta\gamma)$ is established. The assumption of sphericity of nanometric water clusters containing $n > 123$ water molecules is supported by experimental studies, molecular dynamics, and Monte Carlo simulations (e.g., Buch et al., 2004; Chaplin, 2017; Stillinger, 1980).

- The ice contact angle is described using the Young equation of a macroscopic three-phase system (consisting of the embryonic phase $\alpha$, maternal phase $\beta$, and paternal phase $\gamma$) as described in Section 2.2. The physical derivation of the Young equation is based on classical thermodynamics and implies validity of the following assumptions: (i) macroscopicity of the three involved phases (capillarity approximation) and (ii) sphericity of the newly formed embryo. Although the condition of macroscopicity of the maternal and paternal phases is satisfied in the present case, this is not necessarily the case for objects of nanometric sizes like the critical ice embryo. However, according to Gutzow and Schmelzer (1995, Section 6.3.8 therein), clusters in the vicinity of the critical cluster size can be considered “sufficiently large” for application of the capillarity approximation in which case the notion of a specific surface energy is applicable. The authors emphasized that, in most cases of crystallization in glass-forming melt with aggregation numbers of the critical cluster of $n \geq 100$, the classical capillarity approximation may be used, at least qualitatively. As this aggregation number corresponds to the order of magnitude of the aggregation number of critical ice embryos, it is reasonable to conclude that assumption (i) is more or less justified also for ice embryos of the critical size. According to Feistel and Wagner (2005, pp. 111–112), the thermodynamic equilibrium state underlying the physical description of ice is usually that of an “undisturbed hexagonal crystal lattice after all spontaneous processes have passed.” The mass density of hexagonal ice can be calculated from the crystallographic parameters of an elementary
building unit of ice, which is a hexagonal cage containing 27 water molecules with 12 at the corners (in common for the particular six neighboring cells), six on the side edges (shared by three cells each), two in the top and bottom hexagonal face-centered (shared by two cells each), and seven in the prism’s interior, resulting in a total of 12/6 + 6/3 + 2/2 + 7 = 12 water molecules effectively remaining per elementary cell (Feistel and Wagner, 2005, pp. 110–111, Fig. 6 therein). The molar density of hexagonal ice reads [Feistel and Wagner, 2005, Eq. (5.4) therein]:

$$\rho'(\alpha) = \frac{1}{\rho'(\alpha)} = 12 \frac{M_w/N_A}{V_{cell}^{(\alpha)}},$$

where \(\rho'(\alpha)\) and \(\rho'(\alpha)\) are the mass density and specific volume of hexagonal ice, \(M_w = 18.01528 \text{ g mol}^{-1}\) is the molar mass of water, \(N_A = 6.02214086 \times 10^{23} \text{ mol}^{-1}\) the Avogadro constant, and \(V_{cell}^{(\alpha)}\) the volume of an elementary unit cell of hexagonal ice. With \(\rho'(\alpha) \approx 1.085 \text{ dm}^3 \text{ kg}^{-1}\) at \(T \approx 234 \text{ K}\) one obtains for the volume of an elementary ice cell a value of \(V_{cell}^{(\alpha)} \approx 0.389 \times 10^{-27} \text{ m}^3\). A spherical critical ice embryo of radius \(R_{crit}(234 \text{ K}) \approx 1.31 \text{ nm}\) has a volume of \(V_{crit}(234 \text{ K}) \approx 9.41 \times 10^{-27} \text{ m}^3\), which is a factor \(\approx 24\) times larger than the volume \(V_{cell}^{(\alpha)}\) of one elementary hexagonal ice cage. The question is, how does this volume ratio affect the shape of aggregated clusters (i.e. how the hexagonality of the elementary ice cages propagates to agglomerates of these cages with increasing aggregation number \(n\)). MD simulations of ice clusters carried out by Buch et al. (2004, Fig. 1) revealed a pronounced hexagonality of the cluster shape for \(H_2O\) aggregation numbers as low as \(n = 20\), but already an essential sphericity of the cluster shape for \(n = 48\), and a rapid loss of hexagonal features in the cluster structure with further increasing cluster size. In view of these findings, the assumptions of phase macroscopicity and cluster sphericity and the application of the Young equilibrium equation to freezing of water on a kaolinite surface seem to be physically plausible. However, the macroscopic notion of interface energy implies the existence of an infinitely thin interface (represented by an ideal plane) between the mutual bulk phases. Unfortunately, this perception is not applicable to the interface between the critical ice embryo and the catalyzing surface. Instead, the \(\alpha/\beta\) interface must be described as a layer of finite thickness. The corresponding refinement of the theory is considered in the generalized Young equation by applying the concept of disjoining pressure, outlined in Section 2.2.

- The contact region between the ice embryo and the catalyzing substrate is described by a three-media (\(\alpha\beta\gamma\)) sandwich model. The bottom of the ice embryo is separated from the surface of the catalyzing substrate by a thin film with a thickness of molecular size, interpreted as a quasi-liquid layer (QLL). The thinness of the film leads to an excess value of the film surface tension, which originates from overlapping of the molecular forces at both interfaces of the film and is a function of the disjoining pressure (e.g., Adamson and Gast, 1997; Derjaguin, 1955a,b; Derjaguin et al., 1987; Goodrich et al., 1981; Hirasaki and Yang, 2002; Jones et al., 2005; Kroto and Rusanov, 1999; Kuni et al., 1996, 1999, 2001; Napari and Laaksonen, 2003; Rusanov, 1967, 1978, 1996; Rusanov and Shechkin, 2005; Rusanov et al., 1994, 2004, 2009; Sonntag, 1977; Wu, 2003). This approach presumes that the disjoining pressure of the QLL can be described in essentially the same way as the disjoining pressure for liquid films (hereafter called liquid-phase approximation). The disjoining pressure is assumed to originate from electrodynamic, electrostatic, and steric molecular forces.

- Because of to the lack of resilient \textit{a priori} information about the line tension \(\kappa^{(\alpha\beta\gamma)}\) at the contact line of the phases \(\alpha, \beta, \) and \(\gamma\) for the ice/water/kaolinite system, this parameter is considered the most uncertain one in comparison to the other physical parameters used in the interface model presented here. Therefore, \(\kappa^{(\alpha\beta\gamma)}\) serves as a closure parameter of the model, the absolute value and sign of which has to be quantified and compared to sparsely available information about \(\kappa^{(\alpha\beta\gamma)}\) from the literature.

### 2.2 Generalized Young Equation

Starting point of the consideration is the generalized Young equation of a macroscopic three-phase system (consisting of the embryonic phase \(\alpha\), which is nucleated from the maternal phase \(\beta\) on a flat surface of the paternal phase \(\gamma\) with
consideration of the surface roughness and line tension (Krotov and Rusanov, 1999; Rusanov, 1996, 2013; Ščekin et al., 2002):

\[ m^{(\alpha\beta\gamma)} = \cos \theta^{(\alpha\beta\gamma)} = K_S \left( \frac{\sigma^{(\beta\gamma)} - \sigma^{(\alpha\gamma)}}{\sigma^{(\alpha\beta)}} \right) - K_L \left( \frac{\kappa^{(\alpha\beta\gamma)}}{R_c} + \frac{\partial \kappa^{(\alpha\beta\gamma)}}{\partial R_c} \right), \]

\[ K_S = \frac{\tilde{A}^{(\beta\gamma)}}{A^{(\beta\gamma)}}, \quad K_L = \frac{\tilde{L}^{(\alpha\beta\gamma)}}{L^{(\alpha\beta\gamma)}}, \quad R_c = R \sin \theta^{(\alpha\beta\gamma)}. \]

According to Eq. (2), the phase compatibility parameter \( m^{(\alpha\beta\gamma)} \) is decomposed into two contributions: one contribution \( m_0^{(\alpha\beta\gamma)} \) originating from the interface energies of the involved phases and another contribution \( m_\kappa^{(\alpha\beta\gamma)} \) originating from the line tension \( \kappa^{(\alpha\beta\gamma)} \), respectively. The quantities \( R = R_{\text{crit}} \) and \( R_c \) are the radii of the critical ice embryo and the contact line, respectively, and \( K_S \) is the surface roughness factor, defined as the ratio of the microphysically rough (actual) two-phase contact area \( \tilde{A}^{(\beta\gamma)} \) and the apparent visible contact area \( A^{(\beta\gamma)} \). Analogously, the parameter \( K_L \) represents the line roughness factor, defined as the ratio of the microphysical (actual) length of the three-phase contact line \( \tilde{L}^{(\alpha\beta\gamma)} \) and the apparent visible line length \( L^{(\alpha\beta\gamma)} \). To satisfy the model assumption of horizontal homogeneity made in Section 2.1, we set \( K_S = 1 \) and \( K_L = 1 \).

The derivation of Eq. (2) is based on the assumptions that the interface is infinitely thin, and the interface energies are described by their bulk values. However, if the macrophase \( \alpha \) is identified with a newly formed embryo of nanometric size, the thickness of the interface between phases \( \alpha \) and \( \gamma \) cannot be neglected in comparison to the length scale of phase \( \alpha \). The finiteness of the interface between phases \( \alpha \) and \( \gamma \) is described by a thin film of phase \( \beta \), separating the phases \( \alpha \) and \( \gamma \) from each other (Fig. 1). In the case of a thin film, the interface forces from both sides of the film will overlap, leading to the appearance of an excess value of the interface energy \( \Delta \sigma_{\Pi}(\Delta h) \) [Dzyaloshinskii et al., 1961, Eq. (5.6); Krotov and Rusanov, 1999, Section 1.7]:

\[ \sigma^{(\alpha\gamma)} = \sigma^{(\alpha\beta)} + \sigma^{(\beta\gamma)} + \Delta \sigma_{\Pi}(\Delta h), \]

where \( \Delta h \) denotes the film thickness. To simplify the problem, next we want to assume that the line tension contribution \( m_\kappa^{(\alpha\beta\gamma)} \) to the three-phases compatibility parameter \( m^{(\alpha\beta\gamma)} \) in Eq. (2), can be implicitly considered in the specification of the excess value of the interface energy, \( \Delta \sigma_{\Pi}(\Delta h) \), by addition of a residual value. The details and justification of this assumption will be explained below. In Section 5, we will show that this residual part of \( \Delta \sigma_{\Pi}(\Delta h) \) can be assigned to line tension effects, the magnitude and sign of which will be quantified. Inserting Eq. (4) into the expression for \( m^{(\alpha\beta\gamma)} \) as defined in Eq. (2) and neglecting roughness effects, one obtains:

\[ m^{(\alpha\beta\gamma)} = m_0^{(\alpha\beta\gamma)} + m_\kappa^{(\alpha\beta\gamma)} \approx -1 - \frac{\Delta \sigma_{\Pi}(\Delta h)}{\sigma^{(\alpha\beta)}}. \]

From Eqs. (1), (4), and (5) follows a negative value of the ice spreading coefficient, \( S^{(\alpha\beta\gamma)} \):

\[ S^{(\alpha\beta\gamma)} = \sigma^{(\beta\gamma)} - \left( \sigma^{(\alpha\beta)} + \sigma^{(\alpha\gamma)} \right) = \sigma^{(\alpha\beta)} \left( m^{(\alpha\beta\gamma)} - 1 \right) < 0. \]

With neglect of adsorption effects, \( \Delta \sigma_{\Pi}(\Delta h) \) can be determined from the following differential equation (e.g., Krotov and Rusanov, 1999, Section 1.7; Rusanov, 1978, Section 14.4):

\[ \frac{\partial \Delta \sigma_{\Pi}}{\partial \Pi} \approx \Delta h \quad \Rightarrow \quad \Delta \sigma_{\Pi}(\Delta h) \approx \Delta \sigma_{\Pi}(\Delta h \to \infty) + \int_{\Pi(\Delta h \to \infty)}^{\Pi(\Delta h)} \xi \, d\Pi(\xi), \]
where \( \Pi(\Delta h) \) denotes the disjoining pressure. To ensure disappearance of the excess value of the interface energy, \( \Delta \sigma_{\Pi}(\Delta h) \), in the limiting case of a thick film (i.e., at \( \Delta h \to \infty \)), the following boundary conditions must be fulfilled:

\[
\lim_{\Delta h \to \infty} \Delta \sigma_{\Pi}(\Delta h) = 0, \quad \lim_{\Delta h \to \infty} \Pi(\Delta h) = 0, \quad \lim_{\Delta h \to \infty} \Delta h \Pi(\Delta h) = 0.
\] (8)

Representing the disjoining pressure \( \Pi(\Delta h) \) in a very general form as

\[
\Pi(\Delta h) = \Pi_0 f_{\Pi}(\Delta h)
\] (9)

with the characteristic pressure \( \Pi_0 \) and the dimensionless dispatcher function \( f_{\Pi}(\Delta h) \), the partial integration of Eq. (7) with consideration of Eq. (8) leads to

\[
\Delta \sigma_{\Pi}(\Delta h) = \Pi(\Delta h) \Delta h + \int_{\Delta h}^{\infty} \Pi(\xi) d\xi = \Pi_0 \lambda(\Delta h),
\] (10)

\[
\lambda(\Delta h) = \Delta h f_{\Pi}(\Delta h) + \lambda_0(\Delta h), \quad \lambda_0(\Delta h) = \int_{\Delta h}^{\infty} f_{\Pi}(\xi) d\xi.
\] (11)

The quantities \( \lambda(\Delta h) \) and \( \lambda_0(\Delta h) \) denote the general forms of the effective and dispatcher length scales of the molecular interaction, respectively.

### 2.3 Determination of the Excess Interface Energy

#### 2.3.1 General Expression

For application of Eq. (5) to the liquid film between the flat substrate and a curved ice embryo (Fig. 1), the change of the film thickness across the interface region between phases \( \alpha \) and \( \beta \) must be taken into account. This interface region comprises two subregions: (i) a region of “direct” contact, where the bottom of the embryo and the catalyzing surface form parallel planes separated from each other by a minimum distance, and (ii) an outer ring region, in which the embryo surface “departs” more and more from the surface of the catalyzing substrate due to the curvature of the embryo surface. As a consequence of the spherical shape of the ice embryo, the film thickness depends on the contact angle, at which two cases must be distinguished, as follows:
1. **Cryophilic catalyzer:** $0 \leq m^{(\alpha \beta \gamma)} \leq 1$

At this, molecular interactions perform only between infinitesimal surface elements of the two adjacent phases $\alpha$ and $\gamma$ inside the contact area $A_c = \pi R^2_c$. The adjacent phases are separated by a molecular length scale $\varepsilon$, which represents the least possible spacing between the surfaces of the embryo and the plane of the substrate (QLL thickness). At $\Delta h = \varepsilon$, the excess interface energy reads as follows:

$$\Delta \sigma_{\Pi}(0 \leq m^{(\alpha \beta \gamma)} \leq 1) = \Delta \sigma_{\Pi}(\varepsilon).$$  \hfill (12)

The quantity $\Delta \sigma_{\Pi}(\Delta h = \varepsilon)$ can be determined from evaluation of Eq. (10) at the argument $\Delta h = \varepsilon$.

2. **Cryophobic catalyzer:** $-1 \leq m^{(\alpha \beta \gamma)} \leq 0$

In this case, molecular interactions originate from superposition of two contributions:

(i) Molecular interactions in the contact region for cryophilic conditions.

(ii) Molecular interactions in the noncontact region, defined by the ring-shaped zone $R_c \leq r \leq R$ of noncontact adhesion; here, molecular interactions perform along the lines connecting the centers of opposite infinitesimal surface elements of the phases $\alpha$ and $\gamma$, separated by the distance $\Delta h(r)$.

At such conditions, $\Delta \sigma_{\Pi}$ can be interpreted as an effective, area-weighted average value over the cross section of the embryo, $A$ [sum of both the contact area $A_c$ and the noncontact area $(A - A_c)$]:

$$\Delta \sigma_{\Pi}(-1 \leq m^{(\alpha \beta \gamma)} \leq 0) = \frac{1}{A} \left[ A_c \Delta \sigma_{\Pi}(\varepsilon) + (A - A_c) \Delta \sigma_{\Pi}((\Delta h)^{(*)}) \right],$$ \hfill (13)

where $\Delta \sigma_{\Pi}((\Delta h)^{(*)})$ is the excess interface energy at some effective distance $\Delta h^{(*)}$ in the interval $\varepsilon < \Delta h^{(*)} \leq h_0$ (Fig. 1). However, the length $\Delta h^{(*)}$ is not required as a separate parameter of the theory, but instead the term $\Phi_{\Pi} = (A - A_c) \Delta \sigma_{\Pi}((\Delta h)^{(*)})$ must be determined as a whole. Integration of $\Delta \sigma_{\Pi}((\Delta h)(r))$, given by Eqs. (10) and (11), over the ring-shaped noncontact area yields the interaction potential (in physical units of $J$) in the noncontact area:

$$\Phi_{\Pi} \left( m^{(\alpha \beta \gamma)} \right) = \frac{A(R)}{A_c(m^{(\alpha \beta \gamma)})} \int_{A_c(m^{(\alpha \beta \gamma)})}^{A(R)} \Delta \sigma_{\Pi}[(\Delta h)(r)] \, dA(r) = 2\pi \int_{R_c(m^{(\alpha \beta \gamma)})}^{R} \Delta \sigma_{\Pi}[(\Delta h)(r)] \, dr$$ \hfill (14)

$$= \Pi_0 V_{\Pi} \left( m^{(\alpha \beta \gamma)} \right),$$  \hfill (15)

$$V_{\Pi} \left( m^{(\alpha \beta \gamma)} \right) = 2\pi \int_{R_c(m^{(\alpha \beta \gamma)})}^{R} \lambda(\Delta h(r)) \, dr.$$  \hfill (16)

The film thickness $\Delta h(r)$ is defined as the vertical distance between opposite points located at the surfaces of the embryo and substrate planes, and depends on the radial distance $r$ from the perpendicular axis through the center of the embryo:

$$\Delta h(r) = h_0 - \sqrt{R^2 - r^2}, \quad h_0 = \varepsilon + z, \quad z = R \cos(\pi - \theta^{(\alpha \beta \gamma)}) = -R m^{(\alpha \beta \gamma)} > 0.$$  \hfill (16)

The quantities $z$ and $h_0$ are the heights of the center of the embryo above the embryo bottom and above the substrate surface, respectively. Therewith, one can determine the effective length, $\lambda(\Delta h)$, and the volume of molecular interactions, $V_{\Pi} \left( m^{(\alpha \beta \gamma)} \right)$, respectively. According to its physical unit, the quantity $V_{\Pi} \left( m^{(\alpha \beta \gamma)} \right)$...
is a volume, hereafter called the effective volume of molecular interaction. In contrast to the geometrical volume, defined by the noncontact space between the catalyst and the embryo, the interaction volume is a signed value that depends on the shape of the function \( f_T(\Delta h) \).

Considering Eq. (16), the geometric volume of the noncontact space, \( V_0 \), reads as follows:

\[
V_0 \left( m^{(\alpha\beta\gamma)} \right) = 2\pi \int_{R_c(m^{(\alpha\beta\gamma)})}^R \Delta h(r) \, dr = \frac{\pi}{3} R^2 \left[ m^{(\alpha\beta\gamma)} \right]^2 \left( 3\epsilon - R m^{(\alpha\beta\gamma)} \right).
\]

By virtue of the contact angle dependence of the film interface energy according to Eqs. (12) and (13), the Young equation [Eq. (5)] becomes an implicit equation in \( m^{(\alpha\beta\gamma)} \):

\[
m^{(\alpha\beta\gamma)} = \cos \theta^{(\alpha\beta\gamma)} \approx -1 - \frac{\Delta \sigma_{\Pi} \left( m^{(\alpha\beta\gamma)} \right)}{\sigma^{(\alpha\beta)}}.
\]

The quantity \( m^{(\alpha\beta\gamma)} \) is considered here to be known as a fitting parameter (pseudo-observable) from heterogeneous freezing experiments for kaolinite particles, \( \sigma^{(\alpha\beta)}(T) \) is known from an empirical interfacial equation of state, and \( \Delta \sigma_{\Pi} \left( m^{(\alpha\beta\gamma)} \right) \) must be determined from additional empirical constraints and from molecular theory to satisfy Eq. (18), i.e., to close the model. The compliance of the empirical constraint \( m^{(\alpha\beta\gamma)}(T) \), [Eq. (1)], requires \( \Delta \sigma_{\Pi} \left( m^{(\alpha\beta\gamma)} \right) < 0 \) in the temperature range \( 234 \, K \leq T \leq 246 \, K \).

### 2.3.2 Specification of the Ice/Liquid Interface Energy

The ice/water interface energy, \( \sigma^{(\alpha\beta)}(T) \) appearing in Eq. (18), is parametrized according to Jeffery and Austin [1997, Eq. (8), Fig. 8 therein], and is based on laboratory experiments on homogeneous freezing of supercooled water droplets in the temperature range \( 193 \, K < T < T_0 = 273.15 \, K \):

\[
\sigma^{(\alpha\beta)} \approx \sigma^{(\alpha\beta)}_{\infty} \left( 1 - \frac{\Delta \sigma^{(\alpha\beta)}}{\sigma^{(\alpha\beta)}_{\infty}} \right), \quad \sigma^{(\alpha\beta)}_{\infty} = \kappa_T L_M \left[ \rho^{(\alpha)} \right]^{2/3} N_A^{-1/3}, \quad \Delta \sigma^{(\alpha\beta)} = \kappa_\sigma (T - T_0), \quad \kappa_T = 0.32, \quad \kappa_\sigma = 9 \times 10^{-3} \, J \, m^{-2} \, K^{-1}.
\]

The quantity \( \sigma^{(\alpha\beta)}_{\infty} \) denotes the Turnbull expression of the bulk ice/water interface energy (e.g., Turnbull, 1950a,b, 1952; Turnbull and Fisher, 1949), and \( \Delta \sigma^{(\alpha\beta)} \) is a corrective value to fit the observed homogeneous water-to-ice nucleation rates using CNT. Furthermore, \( L_M = L_S - L_V \) denotes the molar melting enthalpy of ice (measured in units of \( J \, mol^{-1} \)), with the molar enthalpies of vaporization of supercooled water, \( L_V \), and sublimation of ice, \( L_S \), taken from Murphy and Koop [2005, Eqs. (9), (5)]. The quantity \( \rho^{(\alpha)} \) denotes the molar density of phase \( \alpha \) (ice), and \( N_A \) is the previously introduced Avogadro constant, respectively. Equation (19) delivers \( \sigma^{(\alpha\beta)}(234 \, K) \approx 25.5 \, mJ \, m^{-2} \) and \( \sigma^{(\alpha\beta)}(242 \, K) \approx 27.2 \, mJ \, m^{-2} \), i.e., the temperature coefficient of the interface energy is positive, \( d\sigma^{(\alpha\beta)} / dT > 0 \), which is supported by computer simulations of the surface free energy of a crystal/liquid interface performed by Baidakov [2012, Eq. (3), Fig. 1], and which is reconcilable with the scaling law for the crystal/liquid interface energy proposed by Skripov and Faizullin [2006, p. 100, Eq. (3.85)]. Extending the Stefan-Skapski-Turnbull relation for the crystal/melt interface energy to nonequilibrium states and combining it with the equilibrium conditions from a generalization of Gibbs’s theory of capillarity, Schmelzer et al. [2016, Eq. (30)] obtained a general scaling law for the specific interface energy of crystal clusters of critical size in dependence on pressure and temperature for small and moderate supercooling, \( \sigma^{(\alpha\beta)}(T, p) / \sigma^{(\alpha\beta)}(T_0, p_0) = L_M(T, p) / L_M(T_0, p_0) \), where \( L_M(T, p) = T \left( s^{(\beta)}(T, p) - s^{(\alpha)}(T, p) \right) \) is the melting enthalpy, and \( s^{(\beta)} \) and \( s^{(\alpha)} \) denote the specific entropies of the liquid and solid phases. The quantities \( T_0 \) and \( p_0 \) are the temperature and pressure of the crystal/melt equilibrium. Taking the
equilibrium value $\sigma^{(\alpha \beta)}(T_0, p_0)$ at atmospheric pressure and $T_0 = 273.16$ K from Eq. (19), and determining $s^{(\alpha)}$ and $s^{(\beta)}$ from the Thermodynamic Equation of Seawater TEOS-10 (Feistel, 2012; Feistel et al., 2010; McDougall et al., 2010; Wright et al., 2010), one obtains $\sigma^{(\alpha \beta)}(234 \text{ K}) \approx 25.32 \text{ mJ m}^{-2}$ and $\sigma^{(\alpha \beta)}(242 \text{ K}) \approx 27.45 \text{ mJ m}^{-2}$, which is very close to the result of the Eq. (19) based on homogeneous freezing experiments.

Interpreting Eq. (19) as $\sigma^{(\alpha \beta)} \approx \sigma^{(\alpha \beta)}(\infty) (1 - 2\delta_T / R)$ (e.g., Gutzow and Schmelzer, 1995; Koenig, 1950; Rusanov, 1978; Schmelzer et al., 2005; Tolman, 1949), one obtains $\delta_T = R\Delta \sigma^{(\alpha \beta)}/(2\sigma^{(\alpha \beta)}(\infty)) \approx 1 \text{ Å}$. From nucleation experiments on water vapor-to-liquid nucleation at $T = (200 - 260) \text{ K}$, Holten et al. [2005, Eq. (18), Fig. 8 therein] derived $\delta_T(246 \text{ K}) \approx 0.23 \text{ Å}$ and $\delta_T(234 \text{ K}) \approx 0.3 \text{ Å}$, respectively. Analyzing experiments on ice nucleation in supercooled water in terms of the CNT and diffuse interface theory (DIT) of crystal nucleation, Gránásy (1995, Table 1 therein) found $\delta_T(246 \text{ K}) \approx 0.84 \text{ Å}$ and $\delta_T(234 \text{ K}) \approx 0.9 \text{ Å}$, respectively. However, interpreting different experimental data on vapor-to-liquid nucleation of water in helium in the temperature range $220 \text{ K} \leq T \leq 260 \text{ K}$, Kalikmanov (2006, Fig. 8 therein) found negative values of the Tolman length, $-0.2 < \delta_T < -0.9 \text{ Å}$.

### 2.3.3 Determination of the Effective Length, Potential, and Volume of Molecular Interaction

The determination of $\Delta \sigma_{\Pi} (m^{(\alpha \beta \gamma)})$, which must satisfy Eq. (18), requires the specification of the disjoining pressure $\Pi(\Delta h)$, Eq. (9), for the evaluation of Eq. (10). The disjoining pressure is a superposition of contributions from different molecular interaction forces, the calculation and direct measurement of which is very challenging and highly uncertain (e.g., Adamson and Gast, 1997; Davis, 1996; French, 2000; French et al., 1995; Hirschfelder et al., 1954; Horn, 1990; Israelachvili, 2011; Schmidt, 1997; Sonntag, 1977; Wilen et al., 1995; Wu, 2001). According to the physical nature of molecular interactions, in the present study two basic types of the dispatcher function $f^{(\Pi)}(\Delta h)$ in Eq. (9) are considered, annotated with the superscripts A and B (Fig. 2):

$$f^{(\Pi)}(A/B)(\Delta h) = \begin{cases} \left( \frac{\epsilon}{\Delta h} \right)^3, & \text{type A interactions,} \\ \exp \left( -\frac{\Delta h}{\Lambda} \right) \cos \left( \frac{a \Delta h}{\Lambda} \right), & \text{type B interactions.} \end{cases}$$

(20)

The characteristic length scale of type A interactions is given by the minimum space $\epsilon$ separating the ice embryo from the substrate, and of type B interactions by the characteristic length scale $\Lambda$, respectively. The quantity $a$ is a

---

**FIG. 2:** Dispatcher function, $f^{(\Pi)}_{A/B}$ according to Eq. (20), as a function of the normalized QLL thickness $\Delta h/D^{(\beta)}$ for $\epsilon = \Lambda = D^{(\beta)}$. Graph A: type A interactions; Graph B1: type B interactions with $a = 0$; Graph B2: type B interactions with $a = 2\pi$

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According to Eq. (5), both the interfacial contribution $m^{(\alpha\beta\gamma)}_\sigma$ and the line tension contribution $m^{(\alpha\beta\gamma)}_\kappa$ to the overall phase compatibility parameter $m^{(\alpha\beta\gamma)}$ are considered in the excess value of the interface energy $\Delta \sigma_{\Pi \lambda}(\Delta h)$. The latter considers electrodynamic, electrostatic, and steric oscillation forces, and in addition, a residual interaction force (subscript X) of type B with $a = 2\pi$, which takes into account other, thus far unspecified forces, inclusive line tension effects [represented by the term $m^{(\alpha\beta\gamma)}_X$]. The consideration of a residual force is motivated by the difficulties in the quantification of molecular forces and the lack of a resilient parametrization of the line tension, $\kappa^{(\alpha\beta\gamma)}$, for the ice/water/kaolinite nucleation system. Introduced in this way, the residual disjoining pressure from an unknown interaction force $X$ serves as a closure quantity for Eq. (18). However, in order to limit the number of additional degrees of freedom introduced into the model, we prescribe the general form of this residual disjoining pressure contribution, $\delta \Pi_X(\Delta h)$, by an *ad hoc* assumption for the shape of the dispatcher function, given in form of $f^{(B)}(\Delta h)$, and a characteristic value of the disjoining pressure, $\delta \Pi_{0X}$, which serves as the closure parameter (see Section 4). Later, we will discuss the implications of this residual contribution, if it would originate solely from the line tension.

With the general form of the dispatcher function given by Eq. (20), one can analytically determine the effective lengths [Eq. (11)], the interaction volumes [Eq. (15)], and the interaction potentials [Eq. (14)], respectively.

### 2.3.4 Determination of the Total Excess Interface Energy of a Thin Film

The final expression of the total excess interface energy of the QLL, $\Delta \sigma_{\Pi \lambda}(m^{(\alpha\beta\gamma)})$, in Eqs. (5), (12), and (13), is obtained from a superposition of the EDF, ESF, SOF, and X contributions, respectively:

$$
\Delta \sigma_{\Pi \lambda,\text{tot}}(m^{(\alpha\beta\gamma)}) = \begin{cases} 
\Delta \sigma_{\Pi \lambda,0}(\epsilon), & 0 \leq m^{(\alpha\beta\gamma)} \leq 1, \\
\frac{1}{A} \left( A_\epsilon \Delta \sigma_{\Pi \lambda,0}(\epsilon) + \phi_{\Pi \lambda,0}(m^{(\alpha\beta\gamma)}) \right), & -1 \leq m^{(\alpha\beta\gamma)} \leq 0,
\end{cases}
$$

(21)

$$
\Delta \sigma_{\Pi \lambda,0}(\epsilon) = \Delta \sigma_{\Pi \lambda,\text{EDF}}^{(A)}(\epsilon) + \Delta \sigma_{\Pi \lambda,\text{ESF}}^{(B)}(\epsilon) + \Delta \sigma_{\Pi \lambda,\text{SOF}}^{(B)}(\epsilon) + \delta \sigma_{\Pi \lambda,X}^{(B)}(\epsilon),
$$

$$
\Delta \sigma_{\Pi \lambda,\text{EDF}}^{(A)}(\epsilon) = \Pi_{0,\text{EDF}}^{(A)}(\lambda_{\text{EDF}}^{(A)}(\epsilon), \\
\Delta \sigma_{\Pi \lambda,\text{ESF}}^{(B)}(\epsilon) = \Pi_{0,\text{ESF}}^{(B)}(\lambda_{\text{ESF}}^{(B)}(\epsilon), \\
\Delta \sigma_{\Pi \lambda,\text{SOF}}^{(B)}(\epsilon) = \Pi_{0,\text{SOF}}^{(B)}(\lambda_{\text{SOF}}^{(B)}(\epsilon), \\
\delta \sigma_{\Pi \lambda,X}^{(B)}(\epsilon) = \delta \Pi_{0X}^{(B)}(\epsilon).
$$

(22)

$$
\phi_{\Pi \lambda,0}(m^{(\alpha\beta\gamma)}) = \phi_{\Pi \lambda,\text{EDF}}^{(A)}(m^{(\alpha\beta\gamma)}) + \phi_{\Pi \lambda,\text{ESF}}^{(B)}(m^{(\alpha\beta\gamma)}) + \phi_{\Pi \lambda,\text{SOF}}^{(B)}(m^{(\alpha\beta\gamma)}) + \delta \phi_{\Pi \lambda,X}^{(B)}(m^{(\alpha\beta\gamma)}),
$$

$$
\phi_{\Pi \lambda,\text{EDF}}^{(A)}(m^{(\alpha\beta\gamma)}) = \Pi_{0,\text{EDF}}^{(A)} V_{\Pi \lambda,\text{edf}}^{(A)}(m^{(\alpha\beta\gamma)}), \\
\phi_{\Pi \lambda,\text{ESF}}^{(B)}(m^{(\alpha\beta\gamma)}) = \Pi_{0,\text{ESF}}^{(B)} V_{\Pi \lambda,\text{esf}}^{(B)}(m^{(\alpha\beta\gamma)}), \\
\phi_{\Pi \lambda,\text{SOF}}^{(B)}(m^{(\alpha\beta\gamma)}) = \Pi_{0,\text{SOF}}^{(B)} V_{\Pi \lambda,\text{ssof}}^{(B)}(m^{(\alpha\beta\gamma)}), \\
\delta \phi_{\Pi \lambda,X}^{(B)}(m^{(\alpha\beta\gamma)}) = \delta \Pi_{0X,0} V_{\Pi \lambda,X}^{(B)}(m^{(\alpha\beta\gamma)}).
$$

(23)

The length scales $\lambda_{\text{EDF}}^{(A)}(\epsilon), \lambda_{\text{ESF}}^{(B)}(\epsilon), \lambda_{\text{SOF}}^{(B)}(\epsilon)$, and $\lambda_{X}^{(\alpha\beta\gamma)}(\epsilon)$ are defined by Eqs. (11) and (20), the surface areas $A$ and $A_\epsilon$ by Eq. (13), and the dependencies of the noncontact interaction volumes $V_{\Pi \lambda,\text{edf}}^{(A)}, V_{\Pi \lambda,\text{esf}}^{(B)}, V_{\Pi \lambda,\text{ssof}}^{(B)}$, and $V_{\Pi \lambda,X}^{(B)}$ on $m^{(\alpha\beta\gamma)}$ by Eqs. (15), (20), and (11), respectively. Therewith, the excess interface energy of the QLL, $\Delta \sigma_{\Pi \lambda}(m^{(\alpha\beta\gamma)})$ according to Eq. (21), is a well-defined function of the ice contact angle.

### 2.3.5 Closure Problem: Determination of Residual Disjoining Pressure

As mentioned above, we consider the scaling value of the residual disjoining pressure, $\delta \Pi_{0X}$, as a closure parameter to reproduce the empirical three-phases compatibility parameter $m^{(\alpha\beta\gamma)}(T)$. Inserting $\Delta \sigma_{\Pi \lambda}(m^{(\alpha\beta\gamma)})$ from Eq. (21),
together with Eqs. (22) and (23) into Eq. (5), one obtains the governing equation for the calculation of the residual value of the characteristic disjoining pressure, \( \delta \Pi_{0X}(m^{(\alpha \beta \gamma)}) \), which serves as the closure parameter to satisfy Eq. (18) if \( m^{(\alpha \beta \gamma)} \) is known from the freezing experiments:

\[
\delta \Pi_{0X} = \begin{cases} 
\frac{1}{\lambda_X^A(\varepsilon)} \left[ (1 + m^{(\alpha \beta \gamma)}) \sigma^{(\alpha \beta)} + \Delta \sigma_{EEDF}(\varepsilon) + \Delta \sigma_{ESF}(\varepsilon) + \Delta \sigma_{SO}(\varepsilon) \right], & \text{for } 0 \leq m^{(\alpha \beta \gamma)} \leq 1 \text{ (contact region)}, \\
- \left[ (1 + m^{(\alpha \beta \gamma)}) A^{(\alpha \beta \gamma)} + A_v \left[ \Delta \sigma_{EEDF}(\varepsilon) + \Delta \sigma_{ESF}(\varepsilon) + \Delta \sigma_{SO}(\varepsilon) \right] \right. \\
+ \left. \Phi_{H}(m^{(\alpha \beta \gamma)}) + \Phi_{ESF}(m^{(\alpha \beta \gamma)}) + \Phi_{SO}(m^{(\alpha \beta \gamma)}) \right] / \left[ A_v + \sigma_{EEDF}(\varepsilon) + \sigma_{ESF}(\varepsilon) + \sigma_{SO}(\varepsilon) \right], & \text{for } -1 \leq m^{(\alpha \beta \gamma)} \leq 0 \text{ (noncontact region)}. 
\end{cases}
\]

Knowing \( \Pi_{0X}, \lambda_A^{(\alpha \beta)}, \) and \( \Pi^{(\alpha \beta)}_X \) (for \( * = \{ \text{EDF, ESF, SOF} \} \)), the corresponding excess interface energies \( \Delta \sigma_{EEDF}, \Delta \sigma_{ESF}, \Delta \sigma_{SO} \) entering Eqs. (22)–(24) can be calculated and therefrom \( \delta \Pi_{0X} \), which satisfies Eq. (18).

### 2.4 Specification of the Disjoining Pressure Contributions

#### 2.4.1 Electrodynamic Forces (Type A Interaction)

The disjoining pressure contribution of electrodynamic forces \( \Pi_{EDF} \) (e.g., Dzyaloshinskii et al., 1961\(^\ddagger\); Israelachvili, 2011; Lifshitz, 1955; London, 1937; Tabor et al., 1969; Wu, 2001) is described using the generalized theory of electromagnetic forces between condensed media developed by Dzyaloshinskii et al. (1961). According to this theory, the interactions between the involved bodies perform by (i) fluctuations of an electromagnetic field, manifested in the appearance of thermal radiation of a body beyond its boundaries, and (ii) quantum fluctuations in the interior of a material medium at absolute zero without thermal radiation. For electrodynamic forces between two phases \( \alpha \) and \( \gamma \) interacting across a third phase \( \beta \), the disjoining pressure \( \Pi_{EDF} \) reads (Israelachvili, 2011, Section 13):\(^\S\)

\[
\Pi_{EDF}(\Delta h) = \Pi_{0,EDF} f_{\Pi}^{(\alpha \beta \gamma)}(\Delta h), \quad \Pi_{0,EDF} = -A^{(\alpha \beta \gamma)}_{H} / 6\pi \varepsilon^3, \quad f^{(\alpha \beta \gamma)}_{\Pi}(\Delta h) = \left( \frac{\varepsilon}{\Delta h} \right)^3, \tag{25}
\]

\[
A^{(\alpha \beta \gamma)}_H \approx \frac{3}{4} \frac{k_B T}{\lambda_X^R} \left( \frac{\varepsilon^{(\alpha)} - \varepsilon^{(\beta)}}{\varepsilon^{(\alpha)} + \varepsilon^{(\beta)}} \right) \left( \frac{\varepsilon^{(\gamma)} - \varepsilon^{(\beta)}}{\varepsilon^{(\gamma)} + \varepsilon^{(\beta)}} \right) + \frac{3\lambda_{EP} \varepsilon}{8 \sqrt{2} / \lambda_{EP} \varepsilon} \left[ \frac{[n_{\text{vis}}^{(\alpha)}]^2 - [n_{\text{vis}}^{(\beta)}]^2][n_{\text{vis}}^{(\gamma)}]^2}{[n_{\text{vis}}^{(\alpha)}]^2 + [n_{\text{vis}}^{(\beta)}]^2][n_{\text{vis}}^{(\gamma)}]^2} \right].
\]

In Eq. (25), the quantity \( \Pi_{0,EDF} \) denotes the scaling value of the disjoining pressure. The quantity \( \varepsilon \) is the minimum spacing between phases \( \alpha \) and \( \gamma \), interpreted as the quasi-liquid layer with thickness equal to the molecule diameter of a volume-equivalent sphere, \( D^{(\beta)} = [6/(\pi N_A \rho^{(\beta)})]^{1/3} = \varepsilon \), where \( \rho^{(\beta)} \) denotes the molar density of phase \( \beta \) (supercooled water). Therewith one obtains \( \varepsilon (234 \text{ K}) \approx 3.9 \AA \) and \( \varepsilon (242 \text{ K}) \approx 3.87 \AA \). The quantity \( A^{(\alpha \beta \gamma)}_H \) is the three-media Hamaker constant\(^\#\) calculated on the basis of the DLP theory [Israelachvili, 2011, Eq. (13.15) therein]. The Hamaker constant depends on the static dielectric constants of the three media, \( \varepsilon^{(\alpha)}, \varepsilon^{(\beta)}, \varepsilon^{(\gamma)} \), and on the corresponding refractive indices in the visible range of the electromagnetic spectrum, \( n_{\text{vis}}^{(\alpha)}, n_{\text{vis}}^{(\beta)}, \) and \( n_{\text{vis}}^{(\gamma)} \). The quantity \( \lambda_{EP} \approx 3 \times 10^{15} \text{s}^{-1} \) denotes the main electronic absorption frequency in the ultraviolet (UV). The Hamaker

\(^\ddagger\)Hereafter abbreviated as DLP theory according to the initials of the names Dzyaloshinskii, Lifshitz, and Pitaevskii.
\(^\S\)The form of the disjoining pressure presented in Eq. (25) follows from Eq. (4.18) in Dzyaloshinskii et al. (1961).
\(^\#\)Here, the superscript \( \alpha \beta \gamma \) denotes the spatial order of interacting phases, where the medium across the interactions perform, \( \beta \), is positioned in the middle.
constant is a superposition of two terms. The first term on the right-hand side of \( A_{\text{H}}^{(\alpha\beta\gamma)} \) is proportional to \( k_B T \) with \( k_B = 1.38064852 \times 10^{-23} \text{ JK}^{-1} \) denoting the Boltzmann constant and originates from thermal fluctuations; the second term is proportional to the Planck constant, \( h_P = 6.62607004 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1} \), but is independent of temperature, i.e., delivering a contribution at absolute zero, which reflects the quantum-mechanical origin of the Lifshitz-van der Waals forces. The Hamaker constant is a signed quantity. Depending on the sequential arrangement of the adjacent materials, one can have either \( A_{\text{H}}^{(\alpha\beta\gamma)} \) > 0, i.e., the disjoining pressure is attractive (\( \Pi < 0 \)), or \( A_{\text{H}}^{(\alpha\beta\gamma)} \) < 0, i.e., the disjoining pressure is repulsive (\( \Pi > 0 \)). The relative dielectric constant of ice, \( \epsilon_i^{(\alpha)} (T) \), is parametrized according to Auty and Cole (1952, Table II therein), delivering \( \epsilon_i^{(\alpha)} (234 \text{ K}) \approx 101.9 \) and \( \epsilon_i^{(\alpha)} (242 \text{ K}) \approx 99.8 \). For the refractive index of ice, a value of \( n_{\text{vis}}^{(\alpha)} \approx 1.31 \) at \( \lambda = 0.59 \mu \text{m} \) and \( \theta = -7^\circ \text{C} \) is used (Warren, 1984, Table 1 therein). The relative dielectric constant of water, \( \epsilon_i^{(\beta)} (T) \), is parametrized with consideration of thin-layer effects (e.g., Boyarskii et al., 2002; Helmy and Natale, 1985; Oliveira et al., 2014; Palmer et al., 1952; West et al., 2003). Here, a sigmoidal form for the distance-dependent relative dielectric constant is used, which was proposed by Smith and Pettit [1994, Eq. (15)]. Evaluating this formula at the charge separation distance \( \Delta h \), with \( \Delta h = \Lambda_s = D^{(\beta)} \), \( \Lambda_s \) denoting the characteristic length scale of dielectric interactions and \( D^{(\beta)} \) the molecular diameter of a volume-equivalent sphere, one obtains \( \epsilon_i^{(\beta)} (T) \approx 0.08 \epsilon_i^{(\beta)} (T) + 0.92 \). Here, \( \epsilon_i^{(\beta)} (T) \) denotes the bulk value of the relative dielectric constant of water (IAPWS, 1997a). Therewith, one obtains \( \epsilon_i^{(\beta)} (234 \text{ K}) \approx 10 \) and \( \epsilon_i^{(\beta)} (242 \text{ K}) \approx 9.2 \). For the refractive index of water, a value of \( n_{\text{vis}}^{(\beta)} \approx 1.33 \) at \( \lambda = 0.589 \mu \text{m} \) and \( \theta = 0^\circ \text{C} \) is used (IAPWS, 1997b). For most minerals in rocks, the bulk static relative dielectric constant is quite low, \( \epsilon_i^{(\gamma)} < 10 \) (e.g., Carmona et al., 2011, p. 37 therein; West et al., 2003). With a sufficient degree of accuracy, dry kaolinite can be treated as an isotropic dielectric with relative dielectric constants varying in the range \( \epsilon_i^{(\gamma)} \approx 2.5 \) – 6.45 (e.g., Balan et al., 2001: \approx 5.014 – 6.237; Boyarskii et al., 2002: \approx 4.5; Kaya, 2001: \approx 4; Korošak et al., 2004: \approx 2.5; Peplinski et al., 1995: \approx 3; Robinson and Batchelor, 1994: \approx 5.24–6.45; Zhao and Yin, 2006: \approx 6). In the present analysis, \( \epsilon_i^{(\gamma)} \approx 6 \) is used. For the refractive index of kaolinite, a value of \( n_{\text{vis}}^{(\gamma)} = 1.62 \) is used (American Elements, 2010). With this parameter setup, one obtains for the ice/water/kaolinite Hamaker constant \( A_{\text{H}}^{(\alpha\beta\gamma)} (234 \text{ K}) \approx -2.03 \text{ zJ} \) and \( A_{\text{H}}^{(\alpha\beta\gamma)} (242 \text{ K}) \approx -1.97 \text{ zJ} \) (\( 1 \text{ zJ} = 10^{-21} \text{ J} \)), i.e., the electrodynamic forces are repulsive with a very weak temperature dependence. Therewith the scaling pressure amounts to \( \Pi_{0,\text{ESF}} (234 \text{ K}) \approx 1.82 \text{ MPa} \) and \( \Pi_{0,\text{ESF}} (242 \text{ K}) \approx 1.8 \text{ MPa} \).

### 2.4.2 Electrostatic Forces (Type B Interaction)

Electrostatic interaction forces (ESF) originate from the acquisition of electrostatic charges by neutral particles upon suspending them in a polar solvent (i.e., a solvent of high dielectric constant such as water). The emerging forces are of repulsive nature. Charge acquisition in a liquid can be realized by different mechanisms (e.g., Horn, 1990; Wu, 2001; Israelachvili, 2011, Section 14.1): (i) permanent structural charge imbalance of the surface originating from charge layering in the substrate or from broken bonds; (ii) differential dissolution of the surface (ionization or dissociation of functional surface groups); (iii) adsorption or desorption of ions from electrolyte solutions onto or from a previously uncharged surface controlled by chemical equilibrium with the surrounding solution; and (iv) charge exchange between two dissimilar surfaces very close together, where charges may hop across from one surface to the other causing electrostatic attraction between the oppositely charged surfaces. Charges emerging on a surface (co-ions) will be balanced out by an equal but oppositely charged region of ions dissolved in the polar medium (counterions). The majority of counterions form a diffuse counterion atmosphere. The surface of co-ion charge plus the diffuse counterion cloud establish a diffuse electric double layer (EDL), which can be approximated by the model of an electric capacitor possessing two rigid plates carrying equal but opposite charges (Israelachvili, 2011, Fig. 14.1). The disjoining pressure originating from electrostatic forces in a bulk electrolyte reservoir of phase \( \beta \) confined between two charged surfaces reads [Israelachvili, 2011, Section 14.16, Eq. (14.55)]:

\[
\Pi_{\text{ESF}} (\Delta h) = \Pi_{0,\text{ESF}} \exp \left( -\frac{\Delta h}{\Lambda_D} \right), \quad \Pi_{0,\text{ESF}} \approx \frac{2\sigma_0^2}{\varepsilon_0 \epsilon_i^{(\beta)}}.
\]
Here, $\sigma_0$ denotes the surface charge density, $\varepsilon_0 = 8.854187817 \times 10^{-12} \text{ F m}^{-1}$ is the dielectric constant of the vacuum, and $\varepsilon_r^{(\beta)}$ the relative dielectric constant of the solution. The quantity $\Lambda_D$ is the Debye length scale, serving as the characteristic length scale of the electrostatic interactions between two charged surfaces [Israelachvili, 2011, Eq. (14.36)]. The special case of one-side surface charging (which corresponds to electroneutrality of the ice/water interface) can be recovered from Eq. (26) by replacing the oppositely charged surface at distance $\Delta h$ with a virtual, neutral surface at the midplane position at distance $\Delta h/2$ from the charged surface. Hence, instead of $\Pi_{\text{ESF}}(\Delta h)$, the disjoining pressure must be taken at the half thickness $L$ of the QLL sandwiched between a charged and an electrically neutral surface, i.e., $\Pi_{\text{ESF}}(L)$ with $L = \Delta h/2$ (Wilén et al., 1995, p. 12,432, left column):

$$
\Pi_{\text{ESF}}(\Delta h) = \Pi_0,_{\text{ESF}} f^{(B)}_\Pi(\Delta h), \quad f^{(B)}_\Pi(\Delta h) = \exp \left( -\frac{\Delta h}{\Lambda_D} \right), \quad \Lambda'_D = 2\Lambda_D.
$$

(27)

The function $f^{(B)}_\Pi(\Delta h)$ is obtained from the general form of the type B dispatcher function, Eq. (20), by setting $a = 0$.

For pure water as electrolyte solution, consisting of neutral water molecules, hydroxid ions ($\text{OH}^-$) (with valence $z_{\text{OH}^-} = -1$ and molarity $c_{\text{OH}^-}$), and hydronium ions ($\text{H}_3\text{O}^+$) (with valence $z_{\text{H}_3\text{O}^+} = +1$ and molarity $c_{\text{H}_3\text{O}^+}$), respectively, the Debye length reads:

$$
\Lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r^{(\beta)} k_B T}{2 N_A e^2 I^{(\beta)}}}, \quad I^{(\beta)} \approx \frac{1}{2} \left[ (c_{\text{H}_3\text{O}^+}) \cdot (z_{\text{H}_3\text{O}^+})^2 + (c_{\text{OH}^-}) \cdot (z_{\text{OH}^-})^2 \right],
$$

$$
K_w(T) \approx \frac{c_{\text{H}_3\text{O}^+} \cdot c_{\text{OH}^-}}{c_\odot}, \quad c_\odot = 1 \text{ mol L}^{-1}.
$$

(28)

Here, $I^{(\beta)}$ denotes the ionic strength (measured in units of mol L$^{-1}$), $K_w$ the dimensionless ionization constant of water at standard molality $m^0 = 1$ mol kg$^{-1}$ (IAPWS, 2007), and $c_\odot$ the molarity of a solute in an infinite-diluted solution serving as a reference state with ideal behavior (measured in units of mol L$^{-1}$). As water is a 1:1 electrolyte solution one has $c_{\text{H}_3\text{O}^+} = c_{\text{OH}^-}$. Owing to the very small self-dissociation of pure water, its ionic strength is very small and assumes values of $I^{(\beta)}(234 \text{ K}) \approx 2.32 \text{ mmol L}^{-1}$ and $I^{(\beta)}(242 \text{ K}) \approx 4.78 \text{ mmol L}^{-1}$, which results in relatively large values of the Debye length, amounting to $\Lambda_D(234 \text{ K}) \approx 2 \mu\text{m}$ and $\Lambda_D(242 \text{ K}) \approx 1.36 \mu\text{m}$. The determination of $\sigma_0$ for natural kaolinite in water is based on a combination of the Gouy–Stern–Grahame theory of the electric double layer (Israelachvili, 2011) and an empirical ion-site binding model of kaolinite (Jiang et al., 2010) (see APPENDIX A). Because of the very low ionic strength of water, the corresponding electric surface charge density is very small and practically independent of temperature, amounting to $\sigma_0(234 \text{ K}) \approx -17.6 \mu\text{C m}^{-2}$ and $\sigma_0(242 \text{ K}) \approx -17.1 \mu\text{C m}^{-2}$, which results in very small values of the scaling pressure, $\Pi_{0,\text{ESF}}(234 \text{ K}) \approx 7 \text{ Pa}$ and $\Pi_{0,\text{EDF}}(242 \text{ K}) \approx 7.2 \text{ Pa}$.

### 3. Steric Oscillation Forces (Type B Interaction)

If the distance between two media is on the order of molecular thickness, then the interactions are essentially geometrically influenced by the molecule size, which results in an oscillating behavior. These oscillations originate from the overlapping of electron clouds upon approaching atoms in a molecule bond, which leads to a disturbance of the energetically preferred shape (and reactivity) of the molecule and molecular ordering of the liquid at the adjacent surfaces (e.g., Horn, 1990; Israelachvili, 2011). In the following, a semi-empirical equation for the disjoining pressure contribution, $\Pi_{\text{SOF}}$, is employed that describes the oscillating forces originating from constructive/destructive interference between the local ordering induced by the boundaries at surface separations below a few molecular diameters [Tarazona and Vicente, 1985; Israelachvili, 2011, Section 15.5, Eq. (15.9) therein]:

$$
\Pi_{\text{SOF}}(\Delta h) = \Pi_{0,\text{SOF}} f^{(B)}_\Pi(\Delta h), \quad \Pi_{0,\text{SOF}} = \rho^{(\beta)} E_B(T), \quad E_B(T) = -N_A k_B T, \quad f^{(B)}_\Pi(\Delta h) = \exp \left( -\frac{\Delta h}{D^{(\beta)}} \right) \cos \left( \frac{2\pi \Delta h}{D^{(\beta)}} \right).
$$

(29)

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Here, \( \rho(\beta) \) denotes the previously introduced molar density of water, determined from the Thermodynamic Equation of Seawater TEOS-10 (Feistel et al., 2010, Feistel, 2012, McDougall et al., 2010, Wright et al., 2010), \( E_B \) the molar Boltzmann energy, and \( D(\beta) \) the molecule diameter of a volume-equivalent sphere, serving as a characteristic length scale of steric interactions. The function \( f_{\Pi}^{(B)}(\Delta h) \) is obtained from the general form of the type B dispatcher function [Eq. (20)] by setting \( a = 2\pi \). With \( E_B(234 \text{ K}) \approx -1.95 \text{ kJ mol}^{-1}, \rho(\beta)(234 \text{ K}) \approx 53.5 \text{ kmol m}^{-3}, \) and \( E_B(242 \text{ K}) \approx -2.01 \text{ kJ mol}^{-1}, \rho(\beta)(242 \text{ K}) \approx 54.6 \text{ kmol m}^{-3} \) one obtains a quite large attractive scaling pressure, \( \Pi_{0,SOF}(234 \text{ K}) \approx -0.104 \text{ GPa} \) and \( \Pi_{0,SOF}(242 \text{ K}) \approx -0.11 \text{ GPa} \).

4. RESIDUAL FORCES (TYPE B INTERACTION)

The residual disjoining pressure, \( \delta \Pi_X(\Delta h) \), is ad hoc parametrized similar to Eq. (29) with the dispatcher function, \( f_{\Pi}^{(B)}(\Delta h) \), given by Eq. (29):

\[
\delta \Pi_X(\Delta h) = \delta \Pi_{0,X} f_{\Pi}^{(B)}(\Delta h), \quad \delta \Pi_{0,X} = \rho(\beta) \delta E_X,
\]

where the characteristic value of the disjoining pressure, \( \delta \Pi_{0,X} \), is expressed in terms of \( \rho(\beta) \) and a characteristic value of the residual molar energy \( \delta E_X \), which comprises all unknown, not explicitly parametrized molecular forces inclusive line tension effects, the values of which must close the interface model.

5. RESULTS

Figure 3 displays the dependence of the interaction volume \( V_{\Pi}^{(AB)} \), Eq. (15), as a function of \( \Theta^{(\alpha\beta\gamma)} \) for EDF, ESF, and SOF interactions. For \( \Theta^{(\alpha\beta\gamma)} < 90 \text{ deg} \), the interaction volume is zero. While the EDF and ESF volumes monotonically increase from \( \Theta^{(\alpha\beta\gamma)} < 90 \text{ deg} \) to \( \Theta^{(\alpha\beta\gamma)} > 111 \text{ deg} \), the SOF volume changes its sign at \( \Theta^{(\alpha\beta\gamma)} > 102 \text{ deg} \), which results from the oscillating behavior of steric forces. The inequality \( \Delta_\Theta \gg \varepsilon \approx D(\beta) \) leads to the relation \( V_{\Pi,ESF} \gg V_{\Pi,EDF} \gg |V_{\Pi,SOF}| \). However, as seen from Fig. 4, the electrostatic interaction potential \( \Phi_{\Pi,ESF} \) is negligibly small compared to the other contributions, which is a consequence of the inequality \( \Pi_{0,ESF} \ll \Pi_{0,EDF} \ll \Pi_{0,SOF} \). Figure 5 shows the excess interface energy \( \Delta \sigma_{\Pi} \) [Eq. (21)] as a function of \( \Theta^{(\alpha\beta\gamma)} \). The largest contribution originates from SOF, \( \Delta \sigma_{\Pi,SOF} \approx -(13 - 16) \text{ mJ m}^{-2} \), followed by the residuum \( \Delta \sigma_{\Pi,X} \approx -(4 - 16) \text{ mJ m}^{-2} \), followed by EDF, \( \Delta \sigma_{\Pi,EDF} \approx 1 \text{ mJ m}^{-2} \), and finally by ESF, \( \Delta \sigma_{\Pi,ESF} \approx 0.025 \text{ mJ m}^{-2} \). The total excess interface energy obeys the inequality \( \Delta \sigma_{\Pi,tot} \) (m\(^{(\alpha\beta\gamma)}\)) < 0 and satisfies the empirical constraint \( m^{(\alpha\beta\gamma)}(T) \), Eq. (1).

The residual molar energy \( \delta E_X = -(0.5 - 2) \text{ kJ mol}^{-1} \) shown in Fig. 6 has the same sign and order of magnitude as the Boltzmann energy \( E_B(T) \), both of which being much lower than the molar H-bond energy for water and ice, \( E_{HB} = -(851) \text{ kJ mol}^{-1} \) (e.g., Atkins, 1996, p. 722 therein; Callister and Rethwisch, 2012, Table 2.3 therein; Coulson and Danielsson, 1954; Geiseler and Seidel, 1977, p. 14 therein; Jorgensen and Madura, 1985, Table 4 therein; Kollman and Allen, 1972; Zielkiewicz, 2005, Table 4 therein). Despite its relative smallness, \( \delta E_X \) strongly affects the dependence \( \Theta^{(\alpha\beta\gamma)}(T) \).

The solid line in Fig. 7 represents \( \Theta^{(\alpha\beta\gamma)}(T) \) calculated from Eqs. (18) and (21) with consideration of the residual energy from Eq. (24). This line is identical with the empirical \( \Theta^{(\alpha\beta\gamma)}(T) \) from Eq. (1), confirming the correctness of the closure calculation. The dashed line shows \( \Theta^{(\alpha\beta\gamma)}(T) \) without consideration of \( \delta \Pi_{0,X} \), resulting in (i) cryophilia in the whole temperature range and (ii) \( d(\Theta^{(\alpha\beta\gamma)})/dT > 0 \), which is in contrast to the observed behavior.

With the knowledge of the excess interface energy originating from the residual molecular interactions, \( \Delta \sigma_{\Pi,X} \), we can rewrite Eq. (18) in the following form:

\[
\begin{align*}
m^{(\alpha\beta\gamma)} = & -1 - \frac{\Delta \sigma_{\Pi} (m^{(\alpha\beta\gamma)})}{\sigma^{(\alpha\beta)}} = \frac{\Delta \sigma_{\Pi,tot} - \Delta \sigma_{\Pi,X}}{\sigma^{(\alpha\beta)}} = m^{(\alpha\beta\gamma)}_\Pi \quad \text{for EDF, ESF, and SOF}; \\
& = \frac{\Delta \sigma_{\Pi,X}}{\sigma^{(\alpha\beta)}} = m^{(\alpha\beta\gamma)}_X.
\end{align*}
\]

Here, we have assigned the EDF, ESF, and SOF contributions of the molecular interactions, given by the difference \( \Delta \sigma_{\Pi,tot} - \Delta \sigma_{\Pi,X} \), to the term \( m^{(\alpha\beta\gamma)}_\Pi \). The residual contribution \( \Delta \sigma_{\Pi,X} \) is assigned to the term \( m^{(\alpha\beta\gamma)}_X \).
Interpretation of Ice Contact Angles

FIG. 3: Interaction volume, $V^{(A/B)}_H$ according to Eq. (15), as a function of the ice contact angle $\theta^{(\alpha\beta\gamma)}$ with consideration of $R(T)$. Graph EDF: electrodynamic type A interactions (Section 2.4.1). Graph ESF: electrostatic type B interactions (Section 2.4.2). Graph SOF: steric type B interactions (Section 3). Note the different scaling factors.

FIG. 4: Interaction potential, $\Phi^{(A/B)}_H$ according to Eq. (14), as a function of the ice contact angle $\theta^{(\alpha\beta\gamma)}$. Graph EDF: electrodynamic type A interactions (Section 2.4.1). Graph ESF: electrostatic type B interactions (Section 2.4.2). Graph SOF: steric type B interactions (Section 3). Graph X: residual type B interactions (Section 4).

virtue of the definition $m^{(\alpha\beta\gamma)}_k$ in Eq. (2) (with the assumption $K_L = 1$) and with consideration of the rearrangement in Eq. (31), we can write:

$$m^{(\alpha\beta\gamma)}_k = -\frac{1}{\sigma^{(\alpha\beta)}} \left( \frac{k^{(\alpha\beta\gamma)}}{R_c} + \frac{\partial k^{(\alpha\beta\gamma)}}{\partial R_c} \right) = -\frac{\Delta \sigma_{\Pi,X}}{\sigma^{(\alpha\beta)}}. \quad (32)$$

Neglecting the curvature dependence of the line tension by assuming $(\partial k^{(\alpha\beta\gamma)}/\partial R_c) \ll (k^{(\alpha\beta\gamma)}/R_c)$, the residual excess interface energy can be tentatively interpreted in terms of the line tension as follows:

$$k^{(\alpha\beta\gamma)} \approx \Delta \sigma_{\Pi,X} R_c. \quad (33)$$

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FIG. 5: Excess interface energy, $\Delta \sigma_{I\Pi}$ according to Eq. (21), as a function of the ice contact angle $\theta^{(\alpha\beta\gamma)}$. Graph EDF: electrodynamic contribution (Section 2.4.1). Graph ESF: electrostatic contribution (Section 2.4.2). Graph SOF: steric oscillation contribution (Section 3). Graph X: residual contribution [Eq. (24), Section 4]. Solid line: total excess interface energy, $\Delta \sigma_{I\Pi,\text{tot}}$ according to Eq. (21).

FIG. 6: Residual molar energy $E_X$ (negative ordinate) and ratio $\delta E_X/E_B$ (positive ordinate) as a function of the ice contact angle $\theta^{(\alpha\beta\gamma)}$.

The line tension (Fig. 8) according to Eq. (33) varies in the range $\kappa^{(\alpha\beta\gamma)} = -(5 - 28) \text{ pN}$ with $d\kappa^{(\alpha\beta\gamma)}/dT < 0$. Using the linearized form of $m^{(\alpha\beta\gamma)}(T)$ derived by Ickes et al. [2017, Eq. (8), Table 1, scheme no. 7 therein], one obtains very similar values, $\kappa^{(\alpha\beta\gamma)} = -(6 - 19) \text{ pN}$. The line tension stiffness increases slightly but gradually from $d\kappa^{(\alpha\beta\gamma)}/d\theta^{(\alpha\beta\gamma)} \approx 0.4 \text{ pN/deg}$ at $\theta^{(\alpha\beta\gamma)} \approx 111 \text{ deg}$ (cryophobia) to $d\kappa^{(\alpha\beta\gamma)}/d\theta^{(\alpha\beta\gamma)} \approx 1.3 \text{ pN/deg}$ at $\theta^{(\alpha\beta\gamma)} \approx 83 \text{ deg}$ (cryophilia). The line energy $\kappa^{(\alpha\beta\gamma)}L^{(\alpha\beta\gamma)}$ decreases with increasing contact line length $L^{(\alpha\beta\gamma)} = 2\pi R_c$ (Fig. 9).

6. DISCUSSION

6.1 Quantification of Line Tension Effects

Because of the lack of empirical data of ice/water/kaolinite compatibility parameters, we discuss our results in the light of previous experiments on heterogeneous vapor-to-liquid nucleation of polar substances on solid surfaces. The
negative temperature coefficient of the ice contact angle reported by Welti et al. (2012) and Ickes et al. (2017) corresponds to the negative temperature coefficient of the contact angle in the water/platinum system, reported by Shi and Dhir (2009) on the basis of molecular dynamics (MD) simulations. Our derived values of $\kappa^{(\alpha\beta\gamma)}$ are within the range of line tensions reported previously for different nanoscopic systems (e.g., Amirfazli and Neumann, 2004; Aveyard and Clint, 1996; Djikaev and Ruckenstein, 2008; Gibbs, 1877; Hienola et al., 2007; Rusanov, 1967, 1978, 1996, 2005; Rusanov et al., 2004; Schimmele et al., 2007; Widom, 1995). According to Schimmele et al. (2007), there exists no rigorous thermodynamic argument for a specific sign of the line tension (as already noted by Gibbs,
As follows from Eq. (2), a negative line tension tends to increase the phase compatibility parameter, i.e., the contact line has the tendency to expand. Negative line tensions, as derived here, were reported for heterogeneous nucleation of water (Winkler et al., 2016, $-10^{-10}$ N), and of $n$-nonane/propanol mixtures (Hienola et al., 2007, $-(0 - 4.5) \times 10^{-10}$ N) on silver nanoparticles in each case (from laboratory experiments), for heterogeneous nucleation of water on dry hexadecane (Scheludko, 1985, $-1.5 \times 10^{-10}$ N), for nucleation of Lennard-Jones nanodrops on solid particles (frozen on a fcc lattice) by means of MD and density functional theory (DFT) simulations (Weijs et al., 2011, Section II D, Fig. 6 therein), and for heterogeneous vapor-to-liquid nucleation on a solid substrate from lattice density functional theory (LDFT) simulations (Liu et al., 2013). The latter study also reveals the decrease of the line energy with increasing droplet circumference (Liu et al., 2013, Fig. 4 therein), found also in the present study. The slight but gradual increase of the line tension stiffness with decreasing contact angle in the present study is at least in qualitative agreement with MD simulations of Kanduč (2017) on the contact angle of a water droplet at a planar surface. 

### 6.2 Uncertainties and Alternative Interpretations

Despite the support from previous studies, our line tension estimation should be interpreted with care because of the uncertainties of the adopted disjoining pressure parametrization (among others, the liquid-phase approximation of the QLL) and in view of other factors influencing freezing catalysis in the ice/water/kaolinite system, which results in a fundamental underdeterminacy of the set of theoretical and empirical constraints on immersion freezing. The analysis of the disjoining pressure contributions in the QLL revealed the validity of the inequality $\Pi_{0,ESF} \ll \Pi_{0,EDF} \ll \Pi_{0,SOF}$, i.e., steric oscillation forces, determined by the Boltzmann energy $E_{\beta}(T)$ according to Eq. (29), primarily control the value of the disjoining pressure in the QLL. Even with consideration of parameter uncertainties, the EDF and ESF contributions to the disjoining pressure can under no circumstances compete with the dominant SOF contribution, the magnitude of which determines the magnitude of the residual contribution $\xi$ that is necessary to close Eq. (18). The parametrization of steric forces, manifested in $\Pi_{SOF}$ according to Eq. (29), does not explicitly include physical parameters of the phase $\alpha$ and $\gamma$, but is solely controlled by QLL parameters (phase $\beta$), i.e., the molar density, $\rho^{(\beta)}$, and the characteristic length scale $D^{(\beta)} = D^{(\beta)}(\rho^{(\beta)})$. Deviations in the molar density of the QLL from its bulk value, $\rho^{(\beta)}$, are not expected to have a significant influence on the value of $\Pi_{SOF}(\Delta h)$. For this reason, we assume that the residual molar energy derived here, $\delta E_X = -(0.5 - 2)$ kJ mol$^{-1}$, is a realistic consequence of the employed model assumptions. Because of their multifaceted manifestation at interfaces involving water phases, H-bondings are a hot candidate for the missing interaction force to close Eq. (18). However, as outlined in Section 5, known values of the molar H-bond energy for water and ice are generally much higher than the values of $\delta E_X$ derived here. Because of the impossibility to decipher the mix of molecular interactions in more detail, it is reasonable to identify the residual interaction with the action of the physically well-defined notion of line tension, $\kappa^{(\alpha \beta \gamma)}$.

Apart from uncertainties in the disjoining pressure parametrization, there are also uncertainties resulting from the characterization of the particle surface. Our interpretation of the empirical ice contact angles is essentially based on the perception of an “ideal, horizontally homogeneous kaolinite surface,” the freezing capability of which can be described as an intraparticle phenomenon by the macroscopic notions of interface energy and line tension. The consequence of this perception is that the ice contact angle and its determining interface energies must be considered as representative values characterizing the particle surface as a whole, i.e., with disregard of any locality. This perception corresponds to the assumptions made by Welti et al. (2012, Section 4.2.1 therein) to derive the ice contact angle using the so-called stochastic model, in which the ice contact angle serves as the sole degree of freedom for fitting.

However, Welti et al. (2012) fitted their data also to three other models, which are called the “contact angle probability density function (PDF) model” with two degrees of freedom (Welti et al., 2012, Section 4.2.2 therein),

---

II In the study of Kanduč (2017), the surface was composed of aliphatic chains terminated by polar hydroxyl groups (at $T = 300$ K) and the surface molecules were arranged in a hexagonal lattice. The surface wettability was controlled by scaling the partial charges of the head groups in terms of a surface polarity parameter ($0 =$ nonpolar surface corresponding to complete hydrophobia; $1 =$ completely polar surface with actual hydroxyl groups corresponding to complete surface wetting).
“active site model” with three degrees of freedom (Welti et al., 2012, Section 4.2.3 therein), and “singular model” with two degrees of freedom (Welti et al., 2012, Section 4.2.4 therein). All four employed models provide a physical link between the observed fraction of frozen droplets and CNT-based or other nucleation metrics. Both the contact angle PDF model and the active site model employ CNT-based expressions for the rate of heterogeneous nucleation, $J_{het}(T, m^{(αβγ)})$, measured in units m$^{-2}$ s$^{-1}$, and take into account the horizontal heterogeneity of the surface of individual particles. In the PDF model, it is assumed, that “the particle surface is smooth and uniform for each particle but differs within an ensemble, i.e., the contact angle differs among the particle population” (Welti et al., 2012, p. 9900 therein). In this model, the authors assumed a log-normal PDF for the contact angle, with the mean value and the variance of the contact angle serving as free parameters for fitting.** The active site model takes into account “that even the surface of individual particles might vary significantly with respect to their mineralogical surface composition and morphology. Therefore, instead having a smooth surface, the model assumes that the aerosol is covered with surface inhomogeneities (active sites). A random distribution of active sites is assumed each having an area of $A = 6 \text{ nm}^2$ over the whole surface of each individual particle. The 6 nm$^2$ corresponds to the cross-sectional area of a critical embryo at 239 K [...]. Each active site is assigned a contact angle” (Welti et al., 2012, p. 9900 therein).

In the active site model, the surface density of contact angles is described by an inverse exponential function with three free fit parameters. The active site model also relies on the employment of CNT. Finally, the singular model “describes ice nucleation on active sites which become active at distinct temperatures. This approach is not based on CNT” (Welti et al., 2012, p. 9900 therein). The key metrics in the singular model is the surface density of sites active at a given temperature, $n_a(T)$, measured in units of m$^{-2}$, which formally replaces the product $J_{het}(T, m^{(αβγ)})$ $\tau_{ind}$ in the calculus of the other models, where $\tau_{ind}$ denotes the induction or residence time of supercooled droplets in the cloud chamber prior to freezing.

At first, Welti et al. (2012, Table 2 therein) assumed temperature independence of the free parameters in all of these four models and reported that each model was able to reproduce the observed fraction of frozen droplets as function of temperature, whereas the PDF, active site, and singular models revealed a lower misfit than the stochastic model. This is not surprising because the former models have two to three degrees of freedom for parameter fitting, while the stochastic model has only one. Second, Welti et al. (2012) reanalyzed their data using the stochastic model with admittance of a temperature dependence of $\theta^{(αβγ)}$. In this case, the authors got an excellent reproduction of their observational data. The price for the good descriptive performance of all employed models, however, is the loss of predictive power due to the (unavoidable) employment of several fitting parameters.

In the case of a monodisperse population of particles with different chemical composition and largely varying physical parameters, the question raises whether the scatter of intrinsically temperature-independent contact angles throughout the population (as assumed in the PDF model of Welti et al., 2012). Can pretend an artificial temperature dependence of a unique contact angle adopted for the whole population. To answer this question, we compare the stochastic model of Welti et al. (2012) with their PDF model. According to Welti et al. [2012, Eqs. (5) and (7) therein], the governing equations for the fractions of frozen particles in both models read:

\[
f_i,\text{stoch} = 1 - \exp \left( - J_{het}(T, \theta(T)) \frac{4\pi R_N^2 \tau_{ind}}{\eta} \right),
\]

\[
f_i,\text{pdf} = 1 - \int_0^\pi p(\xi, \mu, \sigma) \exp \left( - J_{het}(T, \xi) \frac{4\pi R_N^2 \tau_{ind}}{\eta} \right) d\xi,
\]

**A PDF model very similar to the one employed by Welti et al. (2012) was also proposed by Niedermeier et al. (2011), and later modified by Niedermeier et al. (2014) and Niedermeier et al. (2015), respectively. Niedermeier et al. (2015) considered a population of droplets, with each droplet containing a single particle, and all particles having the same size. The authors introduced “a measure for the average number of ice nucleating sites available [...]. Each ice nucleating site is assigned a specific contact angle, based on a Gaussian probability density function (PDF), i.e., the probability of a given contact angle is uniform for each ice nucleating site or in other words the sites are identical in a statistical sense. This PDF [...] is characterized by a mean contact angle [...] and a standard deviation, ...”
where \( f_i^{\text{stoch}} \) and \( f_i^{\text{pdf}} \) are the observed fractions of water droplets, which are frozen out of a population of supercooled water droplets containing an immersed kaolinite particle of radius \( R_\theta \), (i) either characterized by a temperature-dependent ice contact angle \( \theta = \theta(\sigma T) \) (stochastic model), or (ii) by a temperature-independent probability density function of contact angles, \( p_\theta(\theta, \mu, \sigma) \), in the interval \([0, \pi]\) across the particle population (PDF model). Here, \( \mu \) and \( \sigma \) are free parameters of the PDF model. The frozen droplets are formed at a heterogeneous nucleation rate \( J_{\text{het}}(T, \theta) \) during the induction time \( \tau_{\text{ind}} \). As the fraction of frozen droplets is a primary observable, we assume \( f_i^{\text{stoch}} = f_i^{\text{pdf}} \) and try to explain the observations by different approaches. This assumption results in the following equation, where we have introduced the auxiliary constant \( \eta = \pi R_\theta^2 \tau_{\text{ind}}^2 \):

\[
\exp \left( -\eta J_{\text{het}}(T, \theta(T)) \right) = \int_0^\pi p_\theta(\xi, \mu, \sigma) \exp \left( -\eta J_{\text{het}}(T, \xi(T)) \right) d\xi.
\]  

(36)

Differentiation of the left-hand side of Eq. (36) with respect to temperature yields:

\[
\frac{d}{dT} \left[ \exp \left( -\eta J_{\text{het}}(T, \theta(T)) \right) \right] = -\eta \exp \left( -\eta J_{\text{het}}(T, \theta(T)) \right) \left\{ \frac{\partial J_{\text{het}}(T, \theta(T))}{\partial T} \frac{d\theta}{dT} + \frac{\partial J_{\text{het}}(T, \theta(T))}{\partial \theta} \frac{d\theta}{dT} \right\}.
\]  

(37)

Analogously, differentiation of the right-hand side of Eq. (36) with respect to temperature yields:

\[
\frac{d}{dT} \int_0^\pi p_\theta(\xi, \mu, \sigma) \exp \left( -\eta J_{\text{het}}(T, \xi) \right) d\xi = -\eta \int_0^\pi p_\theta(\xi, \mu, \sigma) \exp \left( -\eta J_{\text{het}}(T, \xi) \right) \frac{\partial J_{\text{het}}(T, \xi)}{\partial T} d\xi.
\]  

(38)

Inserting Eqs. (37) and (38) into Eq. (36) and moving the term \( d\theta/dT \) to the left-hand side, one obtains:

\[
\frac{d\theta}{dT} = \frac{\partial J_{\text{het}}(T, \theta)}{\partial T} \left\{ 1 - \int_0^\pi p_\theta(\xi, \mu, \sigma) \exp \left[ \eta (J_{\text{het}}(T, \theta) - J_{\text{het}}(T, \xi)) \frac{\partial J_{\text{het}}(T, \xi)}{\partial T} \right] d\xi \right\}.
\]  

(39)

As the nucleation rate decreases with increasing temperature and increasing contact angle, \( \partial J_{\text{het}}(T, \theta)/\partial T > 0 \) and \( \partial J_{\text{het}}(T, \theta)/\partial \theta < 0 \), one has \( B < 0 \). Hence, the sign of \( d\theta/dT \) depends on the value of \( C \), delivering \( d\theta/dT = 0 \) for \( C = 1 \), \( d\theta/dT > 0 \) for \( C > 1 \), and \( d\theta/dT < 0 \) for \( C < 1 \). The exact value of \( C \), in turn, depends on the shapes of the highly nonlinear functions \( J_{\text{het}}(T, \theta) \) and \( p_\theta(\theta, \mu, \sigma) \), and on the settings of the free parameters \( \mu \) and \( \sigma \) therein. Welti et al. [2012, Eq. (6) therein] assumed a log-normal distribution for \( \theta \):

\[
p_\theta(\theta, \mu, \sigma) = \begin{cases} \frac{1}{\sqrt{2\pi\sigma\theta}} \exp \left( -\frac{(\ln(\theta) - \mu)^2}{2\sigma^2} \right), & \theta > 0, \\ 0, & \theta = 0 \end{cases}.
\]  

(40)

The free parameters \( \mu \) and \( \sigma \) denote the mean and standard deviation of the natural logarithm of the contact angle, \( \ln(\theta) \), and are related to the arithmetic mean of the contact angle, \( \bar{\theta} \), its modal value \( \theta_0 \), and its arithmetic standard deviation, \( \sigma_\bar{\theta} \):

\[
\bar{\theta} = \exp \left( \mu + \frac{\sigma^2}{2} \right), \quad \theta_0 = \exp \left( \mu - \sigma^2 \right) < \bar{\theta}, \quad \sigma_\bar{\theta} = \exp \left( \mu + \frac{\sigma^2}{2} \right) \sqrt{\exp(\sigma^2) - 1}
\]

\[
The \bar{\theta} = \ln \left[ \left( 1 + \frac{\sigma_\bar{\theta}^2}{\bar{\theta}^2} \right) \right] \ln \left[ \theta_0 \left( 1 + \left( \frac{\sigma_\bar{\theta}}{\bar{\theta}} \right)^2 \right) \right], \quad \sigma = \sqrt{\ln \left[ 1 + \left( \frac{\sigma_\bar{\theta}}{\bar{\theta}} \right)^2 \right]}.\]
Assuming a narrow PDF with \( \sigma_0/\bar{\theta} < 1 \) such that \((\sigma_0/\bar{\theta})^2 \ll 1\), one has

\[
\mu = \ln (\bar{\theta}) \approx \ln(\theta_0), \quad \sigma \approx \frac{\sigma_0}{\bar{\theta}}
\]

At the modal value, \( \theta_0 \), the PDF assumes its maximum, which amounts for small \( \sigma_0 \)

\[
p_0(\theta_0, \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(\frac{\sigma^2}{2} - \mu\right) \approx \frac{1}{\sqrt{2\pi}\sigma_0} \exp\left(\frac{\sigma_0^2}{2\bar{\theta}}\right).
\]

By virtue of

\[
\lim_{\sigma_0 \to 0} p_0(\theta_0, \sigma_0) = \infty,
\]

a narrow \( p_0(\theta, \mu, \sigma) \) can be considered an approximation of the Dirac delta function \( \delta_D(x) \) with the convolution property

\[
\int_{-\infty}^{\infty} f(x)\delta_D(x - b) \, dx = f(b), \quad \int_{-\infty}^{\infty} \delta_D(x - b) \, dx = 1,
\]

where \( f(x) \) denotes a real function of argument \( x \). Here, \( b \) serves as a parameter in units of \( x \). With consideration of the convolution property, the term \( C \) in Eq. (39) can be simplified as follows:

\[
C(\theta, \theta_0) \approx \int_{0}^{\infty} \delta_D(\bar{x} - \theta_0) \exp\left[ \eta \left( J_{het}(T, \theta) - J_{het}(T, \bar{x}) \right) \right] \left( \frac{\partial J_{het}(T, \bar{x})}{\partial T} \right)_{\theta_0} \, d\bar{x} = \exp\left[ \eta \left( J_{het}(T, \theta) - J_{het}(T, \theta_0) \right) \right] \left( \frac{\partial J_{het}(T, \theta)}{\partial T} \right)_{\theta_0}.
\]

If the contact angle \( \theta \) derived from the stochastic model will be interpreted as the modal value of a narrow log-normal PDF, \( \theta = \theta_0 \), one has \( D \approx 1 \), \( C(\theta, \theta_0) \approx 1 \), and \( d\theta/dT \approx 0 \) by virtue of Eq. (39). This means that the assumption of a log-normal distribution of the contact angle with temperature-independent parameters \( \theta \) and \( \sigma_0 \) under the constraint \((\sigma_0/\bar{\theta})^2 \ll 1 \) does not counterfeit an artificial temperature dependence of the contact angle, \( \theta^{(\alpha\beta\gamma)}(T) \). Permitting the reverse conclusion, under the condition of a carefully size-selected particle population with homogeneity of chemical composition and uniformity of the physical parameters (reflected in a low value of \( \sigma_0 \)), the best-fitted temperature dependence \( \theta^{(\alpha\beta\gamma)}(T) \) can be considered to represent an intraparticle effect. In contrast to this, the application of the stochastic model with assumption of a single contact angle to a mixed particle population with large interparticle variability (characterized by a wide log-normal distribution of the contact angle) is misleading, because it can counterfeit a temperature dependence \( \theta^{(\alpha\beta\gamma)}(T) \) without physical substantiation. In such a case, the interparticle variability of surface characteristics can easily mask intraparticle molecular interactions at the substrate/embryo interface. As a consequence, mechanistic studies on freezing catalyzes of chemically homogeneous particles pose a great challenge in preparation and physicochemical characterization of the catalyzing particles to exclude interference from interparticle variability.

### 6.3 Implications for Consideration of “Locality” in the Phase-Compatibility Parameter

Welti et al. (2012) demonstrated that both the stochastic model with a temperature-dependent contact angle (interparticle approach) as well as the PDF model with temperature-independent arithmetic mean and standard deviation of the contact angle (interparticle approach) are able to reproduce the observed fraction of frozen droplets as function of temperature. This means that both approaches contain sufficient degrees of freedom to cope with the nonlinearity of immersion freezing rate \( J_{het}(T, \theta) \). A discrimination between intra- and interparticle contributions to \( d\theta^{(\alpha\beta\gamma)}/dT \)
on the base of a quantitative evaluation of Eq. (39) would ideally require an empirical parametrization of the contact angle PDF, $p_\theta(\theta, \sigma_\theta)$, to characterize the microscopic surface heterogeneity. A reduction of the number of fitting parameters necessitates a direct observation of the spatial variation of either the “local contact angle,” its generating “local interface energies” across the particle surface, or suitable proxies. With respect to “representativeness” of the contact angle, it is not clear whether immersion freezing is primarily controlled by the mean, modal, or the minimum value of the ice contact angle. For example, one could tentatively assume that for a given degree of metastability of a homogeneous maternal phase the onset of nucleation occurs most likely at the surface location with the lowest contact angle,†† regardless of the absolute abundance of this location on the surface.†‡ Thus, in the stochastic model with only one free parameter the fitted contact angle might also represent the minimum contact angle, representing the most favored nucleation place on the surface. In any case, a pure mathematical refinement of the description of the contact surface cannot fill the gap torn open by a lack of physical constraints and well-defined observables.

There are further nanoscopic determinants influencing freezing of kaolinite, which must be considered in future studies to improve the freezing metrics of kaolinite:

1. the high affinity of the hydroxylated kaolinite (001) plane to adsorb water monomers (e.g., Hu and Michaelides, 2008; Man-Chao and Jian, 2012);
2. the amphotericism of both the hydroxylated (001) kaolinite surface and water, resulting in a hydro-/cryophilic hydroxylated (001) kaolinite surface, which could explain the formation of a 2D icelike bilayer (with similar energetic stability as hexagonal ice) on the hydroxylated kaolinite surface (e.g., Hu and Michaelides, 2008; Lin and Groß, 2012);
3. the local orientational order of H-atoms in icelike hexagonal bilayers (composed of a water monolayer and an adjacent hydroxylated kaolinite layer);§§
4. the proton affinity of the crystal edges of the (100) planes of kaolinite (Croteau et al., 2008, 2009);∗∗∗
5. the preference of the prism over the basal (hexagonal) plane of ice for crystallite growth on kaolinite (Cox et al., 2013);∗∗∗
6. the nanoscopic roughness of the kaolinite surface (Reinhardt and Doye, 2014).††† the catalyzing effect of

†† Such situation is similar to discharging in a spark gap, which is at given electric field strength more likely to occur for the shortest distance between the two electrodes.
†‡ We recall that only one critical ice germ is required to freeze the whole droplet. It is likely that it forms at the thermodynamic most favored location on the surface of a catalyzing particle, which is completely immersed in a homogeneous metastable maternal phase.
§§ The proton orientation with respect to the catalyzing surface was found to be a key determinant controlling the water affinity and freezing capability of kaolinite. The hydroxylated (001) kaolinite surface prefers a H-down overlayer as its neighbor, in which the protons are oriented toward the substrate surface with full coordination of each water molecule by four H-bonds. The water adsorption energy of the H-down layer amounts to $E_{\text{ads}} = −0.65 \text{eV}/\text{H}_2\text{O}$, which is essentially identical to the cohesive energy of ice Ih, $E_{\text{ads}} = −0.66 \text{eV}/\text{H}_2\text{O}$, resulting in similar thermodynamic stability of water and ice, but that is less than that of the H-up overlayer, $E_{\text{ads}} = −0.48 \text{eV}/\text{H}_2\text{O}$, with reverse orientation of the water molecule (Hu and Michaelides, 2008).
∗∗∗ Croteau et al. (2008) reported the following average adsorption energies for single water molecules at 150 K: $E_{\text{ads}} = (−15.7, −15.6) \text{kJ mol}^{-1}$ for the Si-surface, $E_{\text{ads}} = (−43.1, −41.4) \text{kJ mol}^{-1}$ for the Al-surface, $E_{\text{ads}} = (−69.4, −69.3) \text{kJ mol}^{-1}$ for the unprotonated edges, and $E_{\text{ads}} = (−89.7, −72.0) \text{kJ mol}^{-1}$ for the protonated edges (the two number refer to different water models), revealing a very high water affinity of protonated edges.
***The adsorption energy of the basal face amounts to $E_{\text{ads}} ≈ −0.71 \text{eV}/\text{H}_2\text{O}$, that of the prism plane $E_{\text{ads}} ≈ −0.695 \text{eV}/\text{H}_2\text{O}$, i.e., the basal face of ice is more strongly bound to kaolinite than the basal base.
††† Describing surface roughness by the degree of molecular water penetration into the rigid surface layer, the authors showed a strong dependence of heterogeneous water nucleation on the ratio of the strengths of two- and three-body pairwise molecular interactions in the water/substrate system. For example, the ice contact angle can be significantly increased by reducing the ordering impact of the three-body interaction terms, resulting in a reductions of the tetrahedrality of surface bonding, which disfavors ice nucleation.
trenchlike structures in the kaolinite surface (Croteau et al., 2010b), and the proton order and ferroelectric behavior of water within such trenches (Croteau et al., 2010a).

Sosso et al. (2016a,b) showed the dramatic impact of very small structural changes in the kaolinite surface on the capability of kaolinite to provide a template for the formation of a hexagonal overlayer of water molecules at the water/kaolinite interface. Further effects having a large influence in the freezing capability of a substrate are the crystallographic lattice match (Cox et al., 2012), hydrophilicity of the substrate (Cox et al., 2015a,b), the electric charge distribution (electrofreezing) (Ehre et al., 2010), and possibly nanoscopic pressure effects (e.g., Espinosa et al., 2016; Schmelzer et al., 2016). Our findings on the dominating contribution of steric interaction forces acting on length scales corresponding to the size of molecules are at least in qualitative agreement with the previously reported dramatic impact of tiny structural surface defects on heterogeneous freezing of water on kaolinite.

The essentially correct description of ice nucleation on kaolinite within the framework of CNT (e.g., Ickes et al., 2017; Niedermeier et al., 2015; Sosso et al., 2016a; Welti et al., 2012; Wex et al., 2014) and the rich outcome of computer simulations of the kaolinite/water interface down to nanoscopic scales (e.g., Cox et al., 2013; Croteau et al., 2008, 2009, 2010a,b; Hu and Michaelides, 2008; Sosso et al., 2016b) open new ways for the consideration of local effects in the parametrization of the three-phases compatibility parameter for application of advanced CNT-based approaches to heterogeneous freezing: (i) with consideration of the deliquescence of the catalyzing substrate due to the presence of soluble mass fractions (e.g., Khvorostyanov and Curry, 2004a, 2005, 2014), (ii) with consideration of deviations from the capillarity approximation by generalization of Gibbs’ theory of capillarity (Abyzov et al., 2017), and (iii) with consideration of nanoscopic surface defects (Abyzov et al., 2017). It remains to be investigated how computer simulations of heterogeneous nucleation of water and ice can be used to provide additional constraints for the closure of these theories (e.g., Reinhardt and Doye, 2014; van Enckevort and Los, 2008).

7. CONCLUSIONS

In order to interpret the empirical temperature dependence of the ice contact angle of kaolinite as an intraparticle phenomenon, we performed a closure study on the base of the generalized Young equation in combination with empirical constraints on the disjoining pressure originating from electrodynamic, electrostatic, and steric molecular forces. We derived a negative, temperature-dependent line tension as a closure parameter, which is reconcilable with previous laboratory studies and computer simulations on heterogeneous water nucleation, even though our results are not directly comparable to computer simulations due to differences in the employed catalyzis metrics. The main uncertainty in the interpretation of the observed frozen droplet fraction originates from the degrees of freedom inherent in current CNT-based models of immersion freezing. The underlying model assumptions are physically plausible, but due to lack of physical information, they are not “observationally doubtless.” This concerns, for example, the quantification of the contributions to $\frac{d\alpha}{dT}$, originating from both intra- and interparticle variability of the ice contact angle. A challenge for future studies is the reduction of the number of free parameters in CNT-based approaches to heterogeneous freezing and the development of refined metrics to describe the heterogeneity of particle surfaces, e.g., by consideration of local effects in the three-phases compatibility parameter across the particle surface. Electronic scanning of particle surfaces on nanometric scales and computer simulations can provide additional empirical constraints for the closure of CNT-based freezing models. This would allow one to consider both intra- and interparticle effects in the mechanistic description of water freezing on natural ice nuclei within the framework of CNT.

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Interpretation of Ice Contact Angles


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Interfacial Phenomena and Heat Transfer


Interfacial Phenomena and Heat Transfer


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A.1 Electric Double-Layer Model

According to Israelachvili (2011), the electric double layer is composed of two regions, the Stern layer and the diffuse layer. The Stern layer extends from the solid surface (with charge density $\sigma_s$ and electric potential $\psi_s$) to the inner Helmholtz plane ([IHP]), with charge density $\sigma_i$ and electric potential $\psi_i$. In this layer, the charge and potential distributions are restricted by the geometric size of ions and molecules, and are controlled by interactions between ions and the solid surface. The diffuse layer extends from the IHP to the outer Helmholtz plane ([OHP]), with charge density $\sigma_d$ and electric potential $\psi_d$. In this layer, the potential distribution is governed by the Poisson–Boltzmann equation. Jiang et al. (2010) simplified this model by the following assumptions: (i) the shear potential surface coincides with the OHP ($d\psi(x)/dx = 0$ for all $x < \text{OHP}$), thus $\psi_d = \zeta$ with $\zeta$ denoting the electrostatic potential at the OHP, and (ii) the charge of the solid surface and the Stern layer are combined to yield a net surface charge density $\sigma_0 = \sigma_s + \sigma_i$. The governing equations of the simplified Gouy–Stern–Grahame model read [Israelachvili, 2011, Section 14.11; and Jiang et al., 2010, Eqs. (5), (6)]:

$$\sigma_0 + \sigma_d = 0 \iff \sigma_0 = -\sigma_d, \quad (A.1)$$

$$\sigma_d = -\text{sign}(\sigma_0) \sqrt{2\varepsilon_0\varepsilon_r^0(\beta)} R_u T \sum_i \rho_i^{[\text{br}]i} \left[ \exp \left( -\frac{z_i e \zeta}{k_B T} \right) - 1 \right]. \quad (A.2)$$
Here $\rho_{i,\text{br}}$ denotes the molar density of bulk-reservoir ions (measured in units of mol m$^{-3}$), $R_g = 8.3144598\text{ J} \times \text{mol}^{-1}\text{K}^{-1}$ the universal gas constant, and $e = 1.6021766208 \times 10^{-19}\text{ C}$ the elementary (or electric) charge, respectively. Equation (A.1) represents the condition of electroneutrality of the double layer, and Eq. (A.2) is known as the Grahame equation, relating the surface charge density to the electrostatic surface potential [Israelachvili, 2011, p. 308, Eq. (14.30) therein]. Combining Eqs. (A.1) and (A.2), yields an equation $\sigma_0 = F_{\text{Grahame}}(\zeta)$ for the net surface charge density $\sigma_0$ as a function of the electrostatic potential at the OHP, $\zeta$. The profile of the ion concentration away from the surface is controlled by the Nernst equation and the Boltzmann distribution of the number concentration of bulk-reservoir ions [Israelachvili 2011, p. 308, Eqs. (14.2), (14.25)]. Correspondingly, the ion activities at the OHP and in the bulk also obey the Boltzmann distribution [Jiang et al., 2010, Eq. (7)]:

$$a_s(M^{z_i}) = a_b(M^{z_i}) \exp \left( -\frac{z_i e \zeta}{k_B T} \right),$$

where $a_s(M^{z_i})$ and $a_b(M^{z_i})$ denote the activities of the ion species $M$ with valency $z_i$ (cation or ion) near the surface (OHP) and in the bulk (measured in units of mol m$^{-3}$).

### A.2 Site Binding Model of the Kaolinite/Water Interface

The smallest structural unit of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is a bilayer consisting of a SiO$_4$-tetrahedral layer (t-layer) and a AlO$_6$-octahedral layer (o-layer) (Kézdi, 1969, pp. 83–85) (Fig. A.1). The three basal oxygen atoms of each silicate tetrahedron are joint parts of the basal planes of the two neighboring tetrahedrons, forming a 2D hexagonal network. The fourth apical oxygen-atom of each tetrahedron is not shared by any of the neighboring tetrahedra. Hence, the silicate t-layer comprises a basal oxygen layer, an intermediate silicon layer, and an apical oxygen layer. The aluminate o-layer consists of octahedra, in which one Al-atom is surrounded by six oxygen and hydroxyl (OH) ions. The oxygen atoms that are connected exclusively to aluminium atoms exist as hydroxyl groups. Most of the hydroxyl groups are located in the basal plane of the o-layer. Each hydroxyl group on the basal plane is surrounded by a hexagonal arrangement of six other hydroxyl groups (Hu and Michaelides, 2008). Because of the large abundance of hydroxyl groups in the basal plane of the o-layer, kaolinite is said to “stand on wet feet” (Kaufhold and Dohrmann, 2007). The elementary t- and o-layers are connected via common oxygen atoms (the apical oxygen atoms of the t-layer are linked with the aluminium atoms of the o-layer), and two adjacent o-t bilayers are connected via H-bonds [the hydroxyl (OH$^-$)-terminated (001) face of the o-layer is connected with the oxygen (O$^{2-}$)-terminated (001) face of the t-layer of the adjacent bilayer] (e.g. Hauser-Fuhlberg, 2004, p. 15, Fig. 2.4; Carroll, 1959). The overall charge balance of tetrahedral and octahedral planes of pure kaolinite reveals electroneutrality (Carroll, 1959, p. 753) (Fig. A.1):

![Double layer as the smallest structural unit of kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), consisting of a SiO$_4$-tetrahedral layer (t-layer) and a AlO$_6$-octahedral layer (o-layer), respectively. The elementary t- and o-layers are connected via common oxygen atoms. Redrawn from Kézdi (1969, Fig. 105 therein)](image-url)
The property of the diffuse layer. Therewith, one obtains (Jiang et al., 2010, Table 2):

For this reason, an ideal kaolinite crystal has no permanent surface charges (Kézdi, 1969, p. 84; Fiedler, 2001, p. 24; Hauser-Fühlberg, 2004, p. 6; Kaufhold and Dohrmann, 2007). However, natural kaolinite is assumed to have permanent negative charge sites at its surface, B− (Hauser-Fühlberg, 2004, p. 6; Kaufhold and Dohrmann, 2007). However, natural kaolinite is assumed to have permanent negative charge sites at its surface, B−. Depending on the acidity of the solution, the exposition of surface functional groups at the edges as a result of bond breaking enables the formation of an electric double layer by adsorption/desorption of hydroxyl ions (Missana and Adell, 2000). Structural charging, temporal charging can occur due to the presence of amphoteric surface groups in form of hydroxylated alumina and silica sites of kaolinite, X−OH (with X = {Al, Si} serving as a placeholder), which can either act as a proton donor or proton acceptor in contact with an electrolyte solution. Depending on the acidity of the solution, these amphoteric groups can form either positively charged sites, X−OH+, or negatively charged sites, X−O−, respectively. The proton donor–acceptor reactions on the amphoteric sites read [Jiang et al., 2010, Eqs. (8) and (9)]:

\[
X−OH + H^+ \leftrightarrow X−OH^+, \quad \text{(A.4)}
\]

\[
X−OH \leftrightarrow X−O− + H^+. \quad \text{(A.5)}
\]

Equation (A.4) describes the proton-acceptor reaction, and Eq. (A.5) the proton-donor reaction of alumina and silica sites, respectively. The differential equation of the proton-acceptor reaction (A.4) reads:

\[
\frac{d}{dt}[X−OH^+]_s = K^{(I)}_{X^+} [X−OH]_s [H^+]_s, \\
\frac{d}{dt}[X−OH]_s = K^{(I)}_{X^+} [X−OH^+]_s, \quad \text{(A.6)}
\]

where \( K^{(I)}_{X^+} \) and \( K^{(II)}_{X^+} \) denote the first- and second-order reaction rates (measured in units of s−1 and m2 mol−1 s−1). The subscript s indicates surface values of the ion and molecule concentrations. Symbols in bracket pairs [...]s denote the surface concentration (measured in units of mol m−2). At dynamic equilibrium, the rate of changes of initial and final products are equal:

\[
K'_{X^+} = \frac{K^{(I)}_{X^+}}{K^{(II)}_{X^+}} = \frac{[X−OH]_s [H^+]_s}{[X−OH^+]_s}, \quad \text{(A.7)}
\]

where \( K'_{X^+} \) is the equilibrium constant of the proton-acceptor reaction (measured in units of mol m−2). The proton surface concentration, \( [H^+]_s \), depends on the proton activity at the surface, \( a_s(H^+) \):

\[
[H^+]_s = L_d a_s(H^+). \quad \text{(A.8)}
\]

The property \( L_d \) is the characteristic thickness of the electric double layer (thickness of the Stern layer plus thickness of the diffuse layer). Therewith, one obtains (Jiang et al., 2010, Table 2):

\[
K_{X^+} = \frac{K'_{X^+}}{L_d} = \frac{[X−OH]_s a_s(H^+)}{[X−OH^+]_s} = \frac{[X−OH]_s a_b(H^+)}{[X−OH^+]_s} \exp \left( -\frac{e\zeta}{k_B T} \right), \quad \text{(A.9)}
\]
The quantity $K_{X-}$ is the surface reaction or surface adsorption equilibrium constant for the proton-acceptor reaction (measured in units of mol m$^{-2}$). Analogously, the differential equations of the proton-donor equilibrium (A.5) reads [Jiang et al., 2010, Eq. (25)]:

\[
\begin{align*}
\frac{d}{dt} [\text{Al}^{2+}]_s & = K_{\text{Al}^2+}^\text{(II)} [\text{Al}^+][\text{OH}^-]_s, \\
\frac{d}{dt} [\text{Al}^+]_s & = K_{\text{Al}^+}^\text{(II)} [\text{Al}^{2+}][\text{OH}^-]_s, \\
\end{align*}
\] (A.10)

\[
\sim K'_{X-} = \frac{K_{\text{Al}^2+}^\text{(II)}}{K_{\text{Al}^+}^\text{(II)}} = \frac{[\text{Al}^+][\text{OH}^-]_s}{[\text{Al}^{2+}][\text{OH}^-]_s}.
\] (A.11)

\[
K'_{X-} = \frac{K'_{X-}^\text{d}}{K_{\text{Al}^2+}} = \frac{[\text{Al}^+][\text{OH}^-]_s}{[\text{Al}^{2+}][\text{OH}^-]_s} = \frac{[\text{Al}^+][\text{OH}^-]_s}{[\text{Al}^{2+}][\text{OH}^-]_s} \exp \left(-\frac{e\zeta}{k_B T}\right).
\] (A.12)

The quantity $K'_{X-}$ is the surface reaction or surface adsorption equilibrium constant for the proton-donor reaction (measured in units of mol m$^{-2}$). The closure condition for the determination of the unknown surface charge density $\sigma_0$ is given by the charge-balance equation [Jiang et al., 2010, Eq. (19)]:

\[
\sigma_0(\zeta) = e N_A \left\{ [\text{Al}^{2+}]_s - [\text{Al}^+]_s + [\text{Si}^{-}]_s + [\text{Si}^{2+}]_s - [\text{Si}^{-}]_s - [\text{B}^-]_s \right\},
\] (A.13)

where $N_A$ denotes the Avogadro constant. As empirical constraints balance equations for the surface concentrations of amphoteric alumina and silica sites, $N_{\text{Al}}$ and $N_{\text{Si}}$ (measured in units of mol m$^{-2}$) are considered:

\[
N_{\text{Al}} = [\text{Al}^{2+}]_s + [\text{Al}^{-}]_s + [\text{Al}^{2+}]_s,
\] (A.14)

\[
N_{\text{Si}} = [\text{Si}^{-}]_s + [\text{Si}^{2+}]_s + [\text{Si}^{2+}]_s.
\] (A.15)

Equations (A.9) and (A.12) can be rearranged to obtain the surface concentrations $[\text{Al}^{2+}]_s$ and $[\text{Al}^{-}]_s$ [Jiang et al., 2010, Eqs. (20)–(23)]:

\[
[\text{Al}^{2+}]_s = \frac{[\text{Al}^{2+}]_s a_s(\text{H}^+)}{K_{\text{Al}^+}},
\] (A.16)

\[
[\text{Si}^{2+}]_s = \frac{[\text{Si}^{2+}]_s a_s(\text{H}^+)}{K_{\text{Si}^+}},
\] (A.17)

\[
[\text{Al}^{-}]_s = \frac{[\text{Al}^{-}]_s a_s(\text{H}^+)}{K_{\text{Al}^-}},
\] (A.18)

\[
[\text{Si}^-]_s = \frac{[\text{Si}^-]_s a_s(\text{H}^+)}{K_{\text{Si}^-}}.
\] (A.19)

Inserting Eqs. (A.16) and (A.18) into Eq. (A.14) and resolving the obtained equation for $[\text{Al}^+]_s$ yields [Jiang et al., 2010, Eq. (24)]:

\[
[\text{Al}^+]_s = N_{\text{Al}} / \left[1 + a_s(\text{H}^+) K_{\text{Al}^-} + \frac{a_s^2(\text{H}^+)}{K_{\text{Al}^+} K_{\text{Al}^-}}\right].
\] (A.20)

Inserting Eq. (A.20) into (A.18) and Eq. (A.18) into (A.16) one obtains $[\text{Al}^{2+}]_s$ [Jiang et al., 2010, Eq. (25)]

\[
[\text{Al}^{2+}]_s = N_{\text{Al}} \left\{ \left( \frac{a_s^2(\text{H}^+)}{K_{\text{Al}^+} K_{\text{Al}^-}} \right) / \left(1 + a_s(\text{H}^+) K_{\text{Al}^-} + \frac{a_s^2(\text{H}^+)}{K_{\text{Al}^+} K_{\text{Al}^-}}\right) \right\}.
\] (A.21)
Analogously, inserting Eqs. (A.17) and (A.19) into Eq. (A.15) and resolving the obtained equation for \([\text{Si}^-\text{O}^-]_s\) yields [Jiang et al., 2010, Eq. (26)]:

\[
[\text{Si}^-\text{O}^-]_s = N_{\text{Si}} \frac{1}{1 + \frac{a_w(H^+)}{K_{\text{Si}^-}} + \frac{a_w^2(H^+)}{K_{\text{Si}^-}K_{\text{Si}^+}}}.
\] (A.22)

Finally, inserting Eq. (A.22) into (A.19) and Eq. (A.19) into (A.17) one obtains \([\text{Si}^-\text{OH}_2^+]_s\) [Jiang et al., 2010, Eq. (27)]:

\[
[\text{Si}^-\text{OH}_2^+]_s = N_{\text{Si}} \left\{ \frac{a_w^2(H^+)}{K_{\text{Si}^-}K_{\text{Si}^+}} \right\} \left[ 1 + \frac{a_w(H^+)}{K_{\text{Si}^-}} + \frac{a_w^2(H^+)}{K_{\text{Si}^-}K_{\text{Si}^+}} \right].
\] (A.23)

With \([\text{Al}^-\text{O}^-]_s\), \([\text{Al}^-\text{OH}_2^+]_s\), \([\text{Si}^-\text{O}^-]_s\), and \([\text{Si}^-\text{OH}_2^+]_s\) from Eqs. (A.20)–(A.23) and with consideration of \(a_w(H^+)\) from Eq. (A.3) the right-hand side of the charge balance equation, Eq. (A.13), is a function of the electrostatic surface potential, \(\zeta\), the bulk proton activity of the electrolyte solution, \(a_b(H^+)\), the proton-acceptor and proton-donor reaction constants \(K_{\text{Al}^+}, K_{\text{Si}^+}, K_{\text{Si}^-}\), and \(K_{\text{Si}^-}\), the surface densities of amphoteric sites, \(N_{\text{Al}}\) and \(N_{\text{Si}}\), and the surface density of inert (permanent negatively charged) sites, \([\text{B}^-]_s\), respectively. Therewith, Eq. (A.13) can be written in the form \(\sigma_0 = F_{\text{Site}}(\zeta)\), hereafter called the site-binding equation. With the Grahame and site-binding equations, one has two equations for the determination of the two unknown properties \(\sigma_0\) and \(\zeta\), respectively. For given \(a_b(H^+)\), surface site densities and the dissociation constant, \(\zeta\) can be numerically determined as the root of the transcendental equation

\[
F_{\text{Grahame}}(\zeta) = F_{\text{Site}}(\zeta).
\]

Knowing \(\zeta\), the surface charge density can be determined either from \(\sigma_0 = F_{\text{Grahame}}(\zeta)\) or \(\sigma_0 = F_{\text{Site}}(\zeta)\), respectively. The kaolinite surface site densities, \(N_{\text{Si}}\) and \(N_{\text{Al}}\) (measured in units of mol m\(^{-2}\)), and proton-acceptor and proton-donor reaction constants, \(K_{\text{Al}^+}, K_{\text{Si}^+}, K_{\text{Si}^-}\), and \(K_{\text{Si}^-}\) (measured in units of mol m\(^{-3}\)), respectively, are taken from Jiang et al. (2010, Table 6). The dimensioned proton activity of bulk water, \(a_b(H^+)\), appearing in Eq. (A.3) is given by the following relation:

\[
a_b(H^+) = c_\infty \sqrt{K_w(T)}, \quad c_\infty = 1 \text{ mol L}^{-1}.
\] (A.24)

Here, \(c_\infty\) denotes the standard molarity, and \(K_w(T)\) the dimensionless ionization constant of water (IAPWS, 2007). For kaolinite, the root of \(F_{\text{Grahame}}(\zeta) = F_{\text{Site}}(\zeta)\) must satisfy the conditions \(\sigma_0 < 0\) and \(\zeta < 0\) (e.g., Agrimont, 2017; Carroll, 1959; Fiedler, 2001; Furukawa et al., 2009; Hauser-Fuhlberg, 2004; Ishida et al., 2000; Kaufhold and Dohrmann, 2007; Kézdi, 1969; Missana and Adell, 2000; Novich and Ring, 1984; Robinson and Batchelor, 1994; Schrot and Sposito, 1997; Zhou and Gunter, 1992). With this constraint, only one root for \(\zeta\) exists in the temperature range 234 K \(\leq T \leq 242\) K, amounting to \(\zeta(242\text{ K}) \approx -0.11\) V and \(\zeta(234\text{ K}) \approx -0.14\) V, respectively. Because of the very low ionic strength of water, the corresponding electric surface charge density (either from the Grahame equation or the site-binding equation) is very small and practically independent of temperature, amounting to \(\sigma_0(234\text{ K}) \approx -17.6 \mu\text{C m}^{-2}\) and \(\sigma_0(242\text{ K}) \approx -17.1 \mu\text{C m}^{-2}\).