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Supplement of

Determination of interfacial parameters of a soluble particle in a nonideal solution from measured deliquescence and efflorescence humidities

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Supplementary Material to

"Determination of interfacial parameters of a soluble particle in a nonideal solution from measured deliquescence and efflorescence humidities"

Model description

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S.1   Deliquescence behaviour from Shchekin–Shabaev–Rusanov (SSR) model

S.1.1   Basic scenario and assumptions

Shchekin and Rusanov (2008) and Shchekin et al. (2008; 2013) developed a three-phases model, which is based on the following geometrical, thermodynamical, and physicochemical assumptions (see Fig. 1):

1. In the initial state, the system consists of a solid soluble core of phase γ, which is embedded in a solvent vapour of phase β. The whole system captures the volume V and has the temperature T. In the equilibrium state, the system consists of a droplet, which is embedded in the solvent vapour of phase β, whereas the droplet consists of a partially dissolved residual core (condensation nucleus (CN)) of phase γ enveloped by a thin liquid film of phase α (shell). If the chemical potential of the solvent vapour approaches a certain threshold value, the residual core completely dissolves in the condensing solvent forming a solution droplet. This is the deliquescence transition. If the chemical potential of the solvent vapour decreases below another certain threshold value, a germ of the phase γ will reappear in the droplet and rapidly grow to form a new core. This is the efflorescence transition. The difference in the threshold values leads to a hysteresis effect and causes a "memory effect" during the hydration/dehydration of hygroscopic particles.

2. The volume V, the temperature T, and the number of molecules of every component stay fixed in both states of the system.

3. The initial solid core, its residue, and the equilibrium droplet are assumed to have a spherical form. The surface of the initial core has the radius R_N, its residue the radius R'_N, and the outer surface of the film the radius R. The film thickness is given by $h = R - R'_N$.

4. The liquid film and the solid nucleus are assumed to be incompressible.

5. The vapour/solution surface tension and the solid core/solution and solid core/vapour interfacial energies are assumed to be independent of the solution concentration. As a consequence, the dependence of the disjoining pressure, required to describe the specific properties of a thin liquid film, on the solution concentration is neglected. This is justified by the fact that the solution concentration in thin films is almost constant and approaches the solubility of the nucleus matter at equilibrium with a flat interface between the solid phase of the nucleus substance and the solution.

6. The bulk properties of the liquid phase of solution are assumed to be dependent on the solution concentration, and the solution is nonideal.

S.1.2 Definition of the chemical potentials

The work of droplet formation will be expressed in terms of the Helmholtz free energy F. Employing the definitions of F, the Gibbs free energy G, and the grand potential or the Landau free energy Ω for a system consisting of k compounds, we have:

$$F = U - TS \,, \tag{S-1}$$

$$G = \sum_k \mu_k N_k \,, \tag{S-2}$$

$$\Omega = F - G \,. \tag{S-3}$$

Here, U denotes the energy of the system, S the entropy, N_k the number of molecules of compound k, and μ_k the corresponding molecular chemical potential. By means of these definitions, the Helmholtz free energy of a multicomponent system can be rewritten as follows:

$$F = \sum_k \mu_k N_k + \Omega \,. \tag{S-4}$$

For a system consisting of liquid (α) and vapour (β) phases with an interface the grand potential can be described as the sum of two terms, a volume and a surface term:

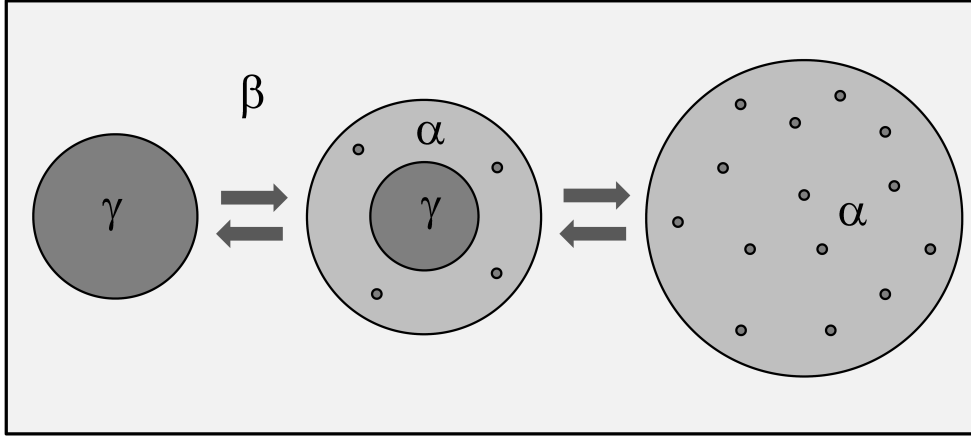$$\Omega^{\{(\alpha),(\beta)\}} = -pV + \sigma A \,. \tag{S-5}$$

Figure 1: Core/shell aggregate in an ambient vapour. Left: initial state; solid soluble core (phase γ) with radius R_{N}, embedded in a solvent vapour (phase β). Middle: equilibrium state I; ambient vapour (phase β) enclosing a droplet with radius R, which consists of a residual core (phase γ) with radius R'_{N} and an enveloping thin liquid film (phase α) with thickness $h = R - R'_{\mathrm{N}}$ (shell). Right: equilibrium state II (deliquescence transition); ambient vapour (phase β) enclosing a solution droplet (phase α) with radius R, corresponding to a completely dissolved residual core at a chemical potential of the solvent vapour above a well-defined threshold value. By decreasing the chemical potential of the solvent vapour below another well-defined threshold value the system moves to the efflorescence transition.

Here, σ denotes the thermodynamic surface tension acting between two mutual phases, and A is the area of that interface.

However, for solid bodies the situation is more complicated. A solid contains necessarily at least one immobile component, which forms a solid lattice. Such immobile component is incapable of diffusion. Therefore, the main mechanism of leveling chemical potentials in vapours and liquids does not work for immobile components in solids (Rusanov et al. 2009). In addition to immobile components, a solid body can also contain mobile components, which freely move inside the solid lattice. These "fluid components" behave as in pure liquid systems including the definition and uniformity of chemical potentials at equilibrium (Rusanov et al. 2009, see references therein). For a uniform bulk phase of a solid (phase γ) consisting only of one immobile (but soluble in the adjacent liquid phase) component, we have (Rusanov et al. 2009, Eq. (33) therein):

$$\Omega^{(\gamma)} \equiv F^{(\gamma)} - \mu^{(\gamma)} N^{(\gamma)} , \quad F^{(\gamma)} = f^{(\gamma)} V^{(\gamma)} , \quad V^{(\gamma)} = v^{(\gamma)} N^{(\gamma)} . \quad \text{(S-6)}$$

Here, $F^{(\gamma)}$ and $f^{(\gamma)}$ denote the free energy and free energy density of the solid (the

latter does not vary upon dissolving a rigid solid), $V^{(\gamma)}$ and $v^{(\gamma)}$ are the volume and partial molecular volume, and $\mu^{(\gamma)}$ and $N^{(\gamma)}$ are the chemical potential and number of molecules of the solid.

In order to determine the work of droplet formation, we start with the specification of the chemical potentials governing the energy balance of the system: the chemical potentials of solvent molecules in the vapour and in the binary liquid film, $\mu^{(\beta)}$ and $\mu^{(\beta \to \alpha)}$, respectively, and the chemical potentials of the solute molecules in the initial core, in the residual core, and in the binary liquid film, $\mu^{(\gamma)}$, $\mu^{(\gamma\prime)}$, and $\mu^{(\gamma \to \alpha)}$, respectively:

1. For an ideal gas, the chemical potential of solvent molecules in the vapour is given by:

$$\boxed{\mu^{(\beta)}\left(p^{(\beta)}\right) = \mu_\infty^{(\beta)}\left(p_\infty^{(\beta)}\right) + k_{\mathrm{B}}T \ln S^{(\beta)} , \quad S^{(\beta)} = \frac{p^{(\beta)}}{p_\infty^{(\beta)}} .} \qquad \text{(S-7)}$$

Here, $\mu_\infty^{(\beta)}$ is the value of the pure condensate chemical potential at the liquid–vapour equilibrium with a flat interface, $S^{(\beta)}$ denotes the vapour saturation ratio (not to be confused with the symbol S for entropy), i. e., the ratio of the actual partial vapour pressure $p^{(\beta)}$ to the equilibrium vapour pressure over a flat surface of the pure solvent (liquid) $p_\infty^{(\beta)}$. The symbol k_{B} is the Boltzmann constant.

2. The chemical potential of the solvent molecules in the liquid film, $\mu^{(\beta \to \alpha)}$, is a function of the pressure $p^{(\alpha)}$ and the relative solute concentration x in the liquid film (Shchekin and Rusanov 2008, Eq. (6) therein):

$$\begin{aligned}
\mu^{(\beta \to \alpha)}\left(p^{(\alpha)}, x\right) &= \mu_0^{(\beta \to \alpha)}\left(p^{(\alpha)}, x \to 0\right) - v^{(\beta \to \alpha)}\pi(x) , \\
v^{(\beta \to \alpha)}\left(p^{(\alpha)}, x\right) &= \left(\frac{\partial \mu^{(\beta \to \alpha)}}{\partial p^{(\alpha)}}\right) .
\end{aligned} \qquad \text{(S-8)}$$

Here, $\mu_0^{(\beta \to \alpha)}\left(p^{(\alpha)}, x \to 0\right)$ denotes the molecular chemical potential of solvent molecules in the pure condensate, $v^{(\beta \to \alpha)}$ is the partial molecular volume of solvent molecules in the liquid, and $\pi(x)$ is the osmotic pressure:

$$\pi(x) = -\frac{k_{\mathrm{B}}T}{v^{(\beta \to \alpha)}(x)} \ln \left[\frac{a_{\mathrm{solvent}}(x)}{a_{\mathrm{solvent}}(x = 0)}\right] . \qquad \text{(S-9)}$$

Here, $a_{\mathrm{solvent}}(x)$ (with $a_{\mathrm{solvent}}(x{=}0){=}1$) is the solvent activity. The osmotic pressure can be interpreted as the *thermodynamic driving force of dilution*

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to reach an infinitely diluted solution[1].

Let $\Delta p = p^{(\alpha)} - p^{(\beta)}$ be the total pressure difference between the liquid and vapour phases. Then Eq. (S-8) can be rewritten (Shchekin and Rusanov 2008, Eq. (7) therein):

$$
\begin{aligned}
\mu^{(\beta\to\alpha)}\left(p^{(\alpha)}, x\right) &= \mu_0^{(\beta\to\alpha)}\left(p^{(\beta)}, x \to 0\right) \\
&\quad + v^{(\beta\to\alpha)}(x)\left[\Delta p - \pi(x)\right] \ .
\end{aligned}
\tag{S-10}
$$

For a thin liquid film of thickness h enveloping a small solid particle, the the mechanical equilibrium between the vapour phase and the film phase is given by the *generalisation of the Laplace equation* (Shchekin and Rusanov 2008, Eq. (9) therein):

$$
\Delta p = p^{(\alpha)} - p^{(\beta)} = \frac{2\sigma^{(\alpha\beta)}}{R} - \left(\frac{R_{\mathrm{N}}}{R}\right)^2 \Pi_{\mathrm{D}}(h) \ , \quad h = R - R_{\mathrm{N}} \ .
\tag{S-11}
$$

In Eq. (S-11), $\sigma^{(\alpha\beta)}$ is the liquid/vapour surface tension of the spherical thin film (not to be confused with the quantity $\sigma_\infty^{(\alpha\beta)}$ for the interface between bulk phases) and Π_{D} is the disjoining pressure, which is defined as follows (Rusanov and Shchekin 2005, Eq. (82) therein):

$$
\Pi_{\mathrm{D}}(h) \equiv p_{\mathrm{N}}^{(\alpha)} - p^{(\alpha)} \ .
\tag{S-12}
$$

Here, $p_{\mathrm{N}}^{(\alpha)}$ denotes the normal component of the pressure tensor inside the spherical liquid film of thickness h, taken at the inner boundary of the film with the spherical residual core. In this study, we will employ the following exponential approximation of the disjoining pressure Π_{D} (Derjaguin et al. 1987; Marčelja and Radić 1976)[2]:

$$
\Pi_{\mathrm{D}}(h) \approx K^{(\star)} \exp\left(-h/l^{(\star)}\right) \ .
\tag{S-13}
$$

---

[1] For example, let us consider an acid fruit (e.g., cherry), enveloped by a pure liquid water film. In order to establish thermodynamic equilibrium between the acid solution and the pure water the osmotic pressure forces the fruit to take up water molecules through the skin (serving as semipermeable membrane). The water uptake leads to a dilution of the fruit solution, but increases the pressure inside the fruit which may burst the skin.

[2] The approximation of Π_{D}, given by Eq. (S-13), was obtained by Marčelja and Radić (1976) for a water film between lecithin bi-layers. At the interface, water molecules assume preferred orientation, while at the same time the rate of molecular motion is severely restricted by the boundaries. The change of ordering leads to the appearance of strong repulsive forces between the boundaries. Consequently, the term Π_{D} represents the structural component of the disjoining pressure. The ordering of water molecules can be described by an order parameter that is related to the free energy via Landau's expansion of the free energy density. By minimising the free energy with consideration of boundary conditions, an analytical expression for the order parameter can be obtained. The determination of the surface excess free energy and its derivation with respect to the layer thickness leads to the expression for the repulsion-induced disjoining pressure on the interfaces, given by Eq. (S-13).

In Eq. (S-13), $K^{(\star)}$ denotes a characteristic pressure scale and $l^{(\star)}$ a characteristic correlation length of the condensation film around the nucleus[3]. The factor $K^{(\star)}$ is related to the spreading coefficient s (Rusanov et al. (1994), Shchekin et al. (1999, Eqs. (12.5)-(12.7)), Tat'yanenko et al. (2000)):

$$K^{(\star)} = s/l^{(\star)} , \quad s = \sigma_\infty^{(\beta\gamma)} - \left(\sigma_\infty^{(\alpha\beta)} + \sigma_\infty^{(\alpha\gamma)}\right) . \qquad \text{(S-14)}$$

Here, $\sigma_\infty^{(\alpha\beta)}$, $\sigma_\infty^{(\alpha\gamma)}$, and $\sigma_\infty^{(\beta\gamma)}$ denote the values of the liquid/vapour, liquid/solid, and vapour/solid surface tensions between the bulk phases. A non-equilibrium spreading coefficient $s>0$ refers to complete wetting of the core surface by a liquid film (in this case, $\sigma_\infty^{(\beta\gamma)}$ is the surface tension of the solid-vacuum interface), $s=0$ to the formation of the equilibrium film and $s<0$ to the disappearance of the film and the formation of a lens-like cluster of the new phase on the surface of the preexisting core (Young equilibrium, contact angle concept). The equilibrium constraint on $\mu^{(\beta\to\alpha)}\left(p^{(\alpha)}, x\right)$ is given by the following equality:

$$\mu_0^{(\beta\to\alpha)}\left(p^{(\beta)}, x \to 0\right) \approx \mu_\infty^{(\beta)} . \qquad \text{(S-15)}$$

Here, the difference $p^{(\beta)} - p_\infty^{(\beta)}$ has been assumed to be much smaller than Δp or $\pi(x)$. For later use we will write $\mu^{(\beta\to\alpha)}\left(p^{(\alpha)}, x\right)$ in the following form:

$$\begin{aligned}
\mu^{(\beta\to\alpha)}\left(p^{(\alpha)}, x\right) &\approx \mu_\star^{(\beta\to\alpha)}(x) + v^{(\beta\to\alpha)}(x)\left(p^{(\alpha)} - p_\infty^{(\beta)}\right) , \\
\mu_\star^{(\beta\to\alpha)}(x) &= \mu_\infty^{(\beta)} + k_B T \ln\left[\frac{a_{\text{solvent}}(x)}{a_{\text{solvent}}(x=0)}\right] .
\end{aligned} \qquad \text{(S-16)}$$

The pressure difference $p^{(\alpha)} - p_\infty^{(\beta)}$ is given by the generalised Laplace equation (S-11).

3. The chemical potential of the solute molecules in the liquid film is obtained in a similar way (Shchekin and Rusanov 2008, Eq. (11) therein):

$$\begin{aligned}
\mu^{(\gamma\to\alpha)}\left(p^{(\alpha)}, x\right) &= \mu_\infty^{(\gamma\to\alpha)}\left(p^{(\alpha)}, x \to x_\infty\right) \\
&\quad - v^{(\gamma\to\alpha)}(x)\,\widetilde{\pi}(x, x_\infty) , \\
v^{(\gamma\to\alpha)}\left(p^{(\alpha)}, x\right) &= \left(\frac{\partial\mu^{(\gamma\to\alpha)}}{\partial p^{(\alpha)}}\right) .
\end{aligned} \qquad \text{(S-17)}$$

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[3] In Landau's theory, $l^{(\star)}$ is the order parameter correlation length, which is of the order of the intermolecular separation. The scaling pressure $K^{(\star)}$ is related to the free energy change associated with ordering the system to the state, given at the interfaces.

In Eq. (S-17), $\mu_\infty^{(\gamma \to \alpha)}\left(p^{(\alpha)}, x \to x_\infty\right)$ denotes the chemical potential of solute molecules in the saturated solution, $v^{(\gamma \to \alpha)}(x)$ is the partial molecular volume of solute molecules in the solution, and $\widetilde{\pi}(x, x_\infty)$ is the *thermodynamic driving force of dissolution* to reach a saturated state of the solution, defined by the solubility of the solute, i.e., the relative solute concentration at saturation of the solution, x_∞. The thermodynamic driving force of dissolution reads:

$$\widetilde{\pi}(x, x_\infty) = -\frac{k_{\mathrm{B}}T}{v^{(\gamma \to \alpha)}(x)} \ln \left[\frac{a_{\mathrm{solute}}(x)}{a_{\mathrm{solute}}(x_\infty)}\right] . \tag{S-18}$$

Here, $a_{\mathrm{solute}}(x)$ is the solute activity.

With the pressure difference $\Delta p = p^{(\alpha)} - p^{(\beta)}$ Eq. (S-17) can be rewritten:

$$\begin{aligned}
\mu^{(\gamma \to \alpha)}\left(p^{(\alpha)}, x\right) &= \mu_\infty^{(\gamma \to \alpha)}\left(p^{(\beta)}, x \to x_\infty\right) \\
&\quad + v^{(\gamma \to \alpha)}(x)\left[\Delta p - \widetilde{\pi}(x, x_\infty)\right] .
\end{aligned} \tag{S-19}$$

The equilibrium constraint on $\mu^{(\gamma \to \alpha)}\left(p^{(\alpha)}, x\right)$ is given by the following equality (see Eq. (S-22), *vide infra*):

$$\mu_\infty^{(\gamma \to \alpha)}\left(p^{(\beta)}, x \to x_\infty\right) = \mu_\infty^{(\gamma)} . \tag{S-20}$$

Therewith for later use we will write $\mu^{(\gamma \to \alpha)}$ in the following form:

$$\boxed{\begin{aligned}
\mu^{(\gamma \to \alpha)}\left(p^{(\alpha)}, x\right) &\approx \mu_\star^{(\gamma \to \alpha)}(x) + v^{(\gamma \to \alpha)}(x)\left(p^{(\alpha)} - p_\infty^{(\beta)}\right) , \\
\mu_\star^{(\gamma \to \alpha)}(x) &= \mu_\infty^{(\gamma)} + k_{\mathrm{B}}T \ln\left[\frac{a_{\mathrm{solute}}(x)}{a_{\mathrm{solute}}(x_\infty)}\right] .
\end{aligned}} \tag{S-21}$$

4. As the equality of the chemical potentials of the core matter inside the spherical solid particle and in the solution breaks, the chemical potentials of the solute in the initial and residual cores cannot be written in a form applicable to vapours and solutions. However, if the value of the chemical potential of the solute in the solution, $\mu^{(\gamma \to \alpha)}\left(p^{(\alpha)}, x\right)$ is known, one can determine the value of the chemical potential of the solid at the core surface, $\mu_\infty^{(\gamma)}$. The equilibrium value of the chemical potential of the solid matter at the flat interface between the solid substrate and a bulk solution at saturation vapour pressure $p_\infty^{(\beta)}$ reads (Shchekin and Rusanov 2008, Eq. (13) therein):

$$\boxed{\mu_\infty^{(\gamma)} = v^{(\gamma)}\left(f^{(\gamma)} + p_{\mathrm{N},\infty}^{(\alpha)}\right) , \quad p_{\mathrm{N},\infty}^{(\alpha)} = p_\infty^{(\beta)} .} \tag{S-22}$$

The quantity $f^{(\gamma)}$ has been introduced above, and $p_{N,\infty}^{(\alpha)}$ is the normal component of the pressure tensor in the film at the boundary with the flat substrate (i. e., at the inner boundary of the film). Therewith and with the help of Eqs. (S-6) and (S-22) the grand potential of a solid can be formally written as:

$$\Omega^{(\gamma)} = -\left[\Delta p^{(\gamma)} + p_\infty^{(\beta)}\right] V^{(\gamma)} \,, \quad \Delta p^{(\gamma)} = \frac{\mu^{(\gamma)} - \mu_\infty^{(\gamma)}}{v^{(\gamma)}} \,. \qquad \text{(S-23)}$$

Via the term $\left(\mu^{(\gamma)} - \mu_\infty^{(\gamma)}\right)/v^{(\gamma)}$ we have formally defined a quantity $\Delta p^{(\gamma)}$ with the dimension of a pressure, which contains information about the thermodynamic state of the solid, and which can be derived for an arbitrarily chosen reference state from the thermal equation of state of the solid (so far available).

For completeness we will also present here the expression for the chemical potential, $\mu^{(\gamma)}\left(p^{(\beta)}\right)$, of the incompressible core matter at the surface of the spherical core with radius R_N under external pressure $p^{(\beta)}$ (Shchekin and Rusanov 2008, see Eq. (12) and references therein):

$$\mu^{(\gamma)}\left(p^{(\beta)}\right) = \mu_\infty^{(\gamma)} + v^{(\gamma)}\left\{\frac{2\sigma_\infty^{(\alpha\gamma)}}{R_N} + \left[\frac{\mathrm{d}\sigma_\infty^{(\alpha\gamma)}}{\mathrm{d}R_N}\right]\right\} \,. \qquad \text{(S-24)}$$

The term $\left[\mathrm{d}\sigma_\infty^{(\alpha\gamma)}/\mathrm{d}R_N\right]$ is the derivative of the surface tension between bulk phases α and γ at a fixed thermodynamic state of the bulk solution.

Finally, we derive the expression for the chemical potential of the solute in the solid, $\mu^{(\gamma)}\left(p_N^{(\alpha)}\right)$, at pressure $p_N^{(\alpha)}$ at the inner boundary of the spherical film around the solid core. At this, we have to replace the surface tension $\sigma_\infty^{(\alpha\gamma)}$ between the bulk phases by the surface tension $\sigma^{(\alpha\gamma)}$ at the inner boundary of the film. In order to specify the derivative $\left[\mathrm{d}\sigma_\infty^{(\alpha\gamma)}/\mathrm{d}R_N\right]$ at pressure $p_N^{(\alpha)}$, we recall that there are differences between the respective surface tensions $\sigma^{(\alpha\beta)}$ and $\sigma^{(\alpha\gamma)}$ at the boundaries of the film and values $\sigma_\infty^{(\alpha\beta)}$ and $\sigma_\infty^{(\alpha\gamma)}$ for the interfaces between bulk phases. The thermodynamics of thin flat films predicts the following relation between the surface tension of a thin film, $\left(\sigma^{(\alpha\beta)} + \sigma^{(\alpha\gamma)}\right)$, and the disjoining pressure $\Pi_D(h)$ (Shchekin and Rusanov 2008, see Eq. (26) and references therein):

$$\frac{\partial\left(\sigma^{(\alpha\beta)} + \sigma^{(\alpha\gamma)}\right)}{\partial h} = -\Pi_D(h) \,. \qquad \text{(S-25)}$$

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Taking into account that the disjoining pressure is determined by the normal component of the pressure tensor at the internal boundary of the film and assuming the main contribution to $\partial \left(\sigma^{(\alpha\beta)} + \sigma^{(\alpha\gamma)} \right) / \partial h$ originating from $\sigma^{(\alpha\gamma)}$, one can approximately replace the surface tension $\sigma^{(\alpha\beta)}$ at the external boundary of the film by its macroscopic value $\sigma_\infty^{(\alpha\beta)}$, i. e., $\sigma^{(\alpha\beta)} \approx \sigma_\infty^{(\alpha\beta)}$. Therewith Eq. (S-25) simplifies to:

$$\frac{\partial \sigma^{(\alpha\gamma)}}{\partial h} \approx -\Pi_D(h) \ . \tag{S-26}$$

Upon integration of Eq. (S-26) at fixed radius R_N from thin film thickness h to thick film thickness $h = \infty$ one arrives at the following expression (Shchekin and Rusanov 2008, Eq. (28) therein):

$$\sigma^{(\alpha\gamma)}(h) \approx \sigma_\infty^{(\alpha\gamma)} + \int_h^\infty \Pi_D(h') \, \mathrm{d}h' \ . \tag{S-27}$$

Here, $\sigma_\infty^{(\alpha\gamma)} = \sigma^{(\alpha\gamma)}(h = \infty)$ denotes the surface tension at the interface of the solid core with the bulk liquid. Keeping the film thickness fixed, we can substantiate the derivation of the $\sigma_\infty^{(\alpha\gamma)}$ as follows:

$$\left[\frac{\mathrm{d}\sigma_\infty^{(\alpha\gamma)}}{\mathrm{d}R_N} \right]_{h=\mathrm{const.}} = \left. \frac{\partial \sigma^{(\alpha\gamma)}}{\partial R_N} \right|_{h=\mathrm{const.}} \ . \tag{S-28}$$

In the general case, the thermodynamic state of a thin film does not only depend on the film thickness, but also on the curvature of each of the film boundaries, because the latter can be varied independently. Fixing only the film thickness is an approximation in that the size of the solid core is assumed to be large in comparison with the molecular size. The condition of a fixed film thickness is, however, strictly valid only for a flat film. Upon adding the pressure difference $\Delta p_N^{(\alpha)}$ between the normal components of the pressure tensor at the inner and outer film boundaries,

$$\Delta p_N^{(\alpha)} = p_N^{(\alpha)} - p^{(\beta)} = p_N^{(\alpha)} - p_{N,\infty}^{(\alpha)} \ ,$$

to the pressure $p^{(\beta)}$, the chemical potential of the solute in the solid reads in accordance with Eq. (S-24):

$$\mu^{(\gamma)} \left(p_N^{(\alpha)} \right) \approx \mu_\infty^{(\gamma)} + v^{(\gamma)} \Delta p_N^{(\alpha)} + v^{(\gamma)} \left\{ \frac{2\sigma^{(\alpha\gamma)}}{R_N} + \left. \frac{\partial \sigma^{(\alpha\gamma)}}{\partial R_N} \right|_{h=\mathrm{const.}} \right\} \ . \tag{S-29}$$

By virtue of Eqs. (S-11), (S-12), and (S-20), one arrives finally at the following expression for $\mu^{(\gamma)}\left(p_{\mathrm{N}}^{(\alpha)}\right)$ from Eq. (S-29) (Shchekin and Rusanov 2008, Eq. (18) therein):

$$
\begin{aligned}
\mu^{(\gamma)}\left(p_{\mathrm{N}}^{(\alpha)}\right) \;\approx\; & \mu_{\infty}^{(\gamma \to \alpha)}\left(p^{(\beta)}, x_{\infty}\right) \\
& +v^{(\gamma)}\left\{\Pi_{\mathrm{D}}+\frac{2\sigma_{\infty}^{(\alpha\beta)}}{R}-\left(\frac{R_{\mathrm{N}}}{R}\right)^{2}\Pi_{\mathrm{D}}\right. \\
& \left.+\frac{2\sigma^{(\alpha\gamma)}(h)}{R_{\mathrm{N}}}+\left.\frac{\partial\sigma^{(\alpha\gamma)}}{\partial R_{\mathrm{N}}}\right|_{h=\mathrm{const.}}\right\}.
\end{aligned}
\tag{S-30}
$$

S.1.3   Work of droplet formation

The work of droplet formation, ΔF, is given by the difference of the Helmholtz free energies between the final and the initial states of the system, F_{final} and F_{initial}:

$$
\Delta F \equiv F_{\mathrm{final}} - F_{\mathrm{initial}} .
\tag{S-31}
$$

The Helmholtz free energy of the initial state, F_{initial}, is given by Shchekin et al. (2008, Eq. (2) therein):

$$
F_{\mathrm{initial}} = \underbrace{\mu^{(\beta)}N_{0}^{(\beta)}}_{\mathrm{initial\,phase\,}\beta} + \underbrace{\mu^{(\gamma)}N_{0}^{(\gamma)}}_{\mathrm{initial\,phase\,}\gamma} + \Omega_{\mathrm{initial}} .
\tag{S-32}
$$

The variables $\mu^{(\beta)}$ and $N_{0}^{(\beta)}$ denote the molecular chemical potential and the initial number of solvent molecules in the vapour, $\mu^{(\gamma)}$ and $N_{0}^{(\gamma)}$ are the molecular chemical potential and initial number of solute molecules in the solid soluble core, and $\Omega_{\mathrm{initial}}$ denotes the grand potential of the system in the initial state, respectively (Shchekin et al. 2008, Eq. (4) therein):

$$
\Omega_{\mathrm{initial}} = \underbrace{-p^{(\beta)}\left(V-V_{R_{\mathrm{N}}}\right)+4\pi R_{\mathrm{N}}^{2}\sigma^{(\beta\gamma)}}_{=\,\Omega_{\mathrm{initial}}^{(\beta)}} + \underbrace{f^{(\gamma)}V_{R_{\mathrm{N}}}-\mu^{(\gamma)}N_{0}^{(\gamma)}}_{=\,\Omega^{(\gamma)}} .
\tag{S-33}
$$

In the final state, a number $\Delta N^{(\beta \to \alpha)}$ out of $N_{0}^{(\beta)}$ molecules has been moved from the vapour phase β to the liquid phase α by condensation, and a number $\Delta N^{(\gamma \to \alpha)}$ out of $N_{0}^{(\gamma)}$ substrate molecules has been moved from the solid phase γ to the liquid phase α by dissolution. Thus, the number of molecules in the residual vapour and solid phases, $N^{(\beta)}$ and $N^{(\gamma)}$, and in the newly emerging liquid phase,

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$N^{(\alpha)}$, read:

$$
\begin{aligned}
N^{(\beta)} &= N_0^{(\beta)} - \Delta N^{(\beta \to \alpha)} \ , \\
N^{(\gamma)} &= N_0^{(\gamma)} - \Delta N^{(\gamma \to \alpha)} \ , \\
N^{(\alpha)} &= \Delta N^{(\beta \to \alpha)} + \Delta N^{(\gamma \to \alpha)} \ .
\end{aligned}
$$

The relative solute concentration in the film, x, and the corresponding molality[4], $m(x)$, are defined as follows:

$$
\begin{aligned}
x &= \frac{\Delta N^{(\gamma \to \alpha)}}{\Delta N^{(\alpha)}} = \frac{\Delta N^{(\gamma \to \alpha)}}{\Delta N^{(\gamma \to \alpha)} + \Delta N^{(\beta \to \alpha)}} \ , \\
m(x) &= \frac{\Delta N^{(\gamma \to \alpha)}/N_A}{M_W \Delta N^{(\beta \to \alpha)}/N_A} = \frac{x}{M_W(1-x)} \ .
\end{aligned}
\tag{S-34}
$$

Here, N_A is the Avogadro constant. For an aqueous solution the solvent is water with molar mass M_W.

Therewith the Helmholtz free energy of the final state, F_{final}, reads (Shchekin et al. 2008, Eq. (3) therein):

$$
\begin{aligned}
F_{\text{final}} = &\underbrace{\mu^{(\beta)} N^{(\beta)}}_{\text{residual phase } \beta} + \underbrace{\mu^{(\gamma')} N^{(\gamma)}}_{\text{residual phase } \gamma} \\
&+ \underbrace{\left(\mu^{(\beta \to \alpha)} \Delta N^{(\beta \to \alpha)} + \mu^{(\gamma \to \alpha)} \Delta N^{\gamma \to \alpha} \right)}_{\text{new phase } \alpha} + \Omega_{\text{final}} \ .
\end{aligned}
\tag{S-35}
$$

In Eq. (S-35), the variables $\mu^{(\gamma')}$, $\mu^{(\beta \to \alpha)}$, and $\mu^{(\gamma \to \alpha)}$ are the molecular chemical potentials of the residual core matter, of the solvent molecules in the liquid phase, and of the solute molecules in the liquid phase. The term Ω_{final} denotes the grand potential of the system in the final state (Shchekin et al. 2008, Eq. (5) therein):

$$
\begin{aligned}
\Omega_{\text{final}} = &\underbrace{-p^{(\beta)} \left(V - V_R \right)}_{= \Omega_{\text{final}}^{(\beta)}} \\
&\underbrace{-p^{(\alpha)} \left(V_R - V_{R_N'} \right) + 4\pi R^2 \sigma_\infty^{(\alpha\beta)} + 4\pi R_N'^2 \sigma_\infty^{(\alpha\gamma)} + \Omega_\Pi}_{= \Omega_{\text{final}}^{(\alpha)}} \\
&+ \underbrace{f^{(\gamma)} V_{R_N'} - \mu^{(\gamma')} N^{(\gamma)}}_{= \Omega^{(\gamma')}} \ .
\end{aligned}
\tag{S-36}
$$

The term Ω_Π appearing in Eq. (S-36) describes the thermodynamic contribution of the disjoining pressure Π_D to the grand potential of a thin liquid film, which

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[4]The molality of a solution, m, is defined as the amount of substance of solute (in mol), n_{solute}, divided by the mass of the solvent (in kg), m_{solvent}.

results from overlapping of the surface layers from the opposite sides of the film (Shchekin et al. 2008, Eq. (16) therein):

$$\Omega_\Pi = 4\pi R_N'^2 \int\limits_h^\infty \Pi(h')\,\mathrm{d}h' \ . \tag{S-37}$$

The aggregation geometry is defined by the radii of the initial and residual cores and by the radius of the droplet, R_N, R_N', and R with their corresponding volumes V_{R_N}, $V_{R_N'}$, and V_R. The volume V_R of the droplet can be represented as[5]:

$$V_R = V_{R_N'} + v^{(\beta\to\alpha)}(x)\,\Delta N^{(\beta\to\alpha)} + v^{(\gamma\to\alpha)}(x)\,\Delta N^{(\gamma\to\alpha)} \ . \tag{S-38}$$

As a result, the number of solvent molecules condensed in the film reads:

$$\Delta N^{(\beta\to\alpha)} = \frac{V_R - V_{R_N'} - v^{(\gamma\to\alpha)}(x)\,\Delta N^{(\gamma\to\alpha)}}{v^{(\beta\to\alpha)}(x)} \ . \tag{S-39}$$

Employing the assumption of sphericity, the volumes of the droplet, of the initial, and of the residual core are given by:

$$V_R = \frac{4\pi}{3}R^3 \ , \quad V_{R_N} = \frac{4\pi}{3}R_N^3 \ , \quad V_{R_N'} = \frac{4\pi}{3}R_N'^3 \ . \tag{S-40}$$

Correspondingly, the numbers of solute molecules in the initial and residual cores as well as in the solution film read:

$$N_0^{(\gamma)} = \frac{4\pi R_N^3}{3v^{(\gamma)}} \ , \quad N^{(\gamma)} = \frac{4\pi R_N'^3}{3v^{(\gamma)}} \ , \quad \Delta N^{(\gamma\to\alpha)} = \frac{4\pi}{3v^{(\gamma)}}\left(R_N^3 - R_N'^3\right) \ . \tag{S-41}$$

Inserting Eqs. (S-32), (S-33) and Eqs. (S-35), (S-36) into Eq. (S-31), and considering Eqs. (S-16) and (S-21) for $\mu^{(\beta\to\alpha)}$ and $\mu^{(\gamma\to\alpha)}$, respectively, one arrives at the following expression for the work of droplet formation on a partially dissolved core:

$$
\begin{aligned}
\Delta F &= -\Delta N^{(\beta\to\alpha)}\left[\mu^{(\beta)} - \mu_\star^{(\beta\to\alpha)}\right] + \Delta N^{(\gamma\to\alpha)}\left[\mu_\star^{(\gamma\to\alpha)} - \mu_\infty^{(\gamma)}\right] \\
&\quad + 4\pi R^2\sigma_\infty^{(\alpha\beta)} + \Delta F_W + \left(p^{(\beta)} - p_\infty\right)\left(V_R - V_{R_N}\right) \ , \\
\Delta F_W &= 4\pi R_N'^2\sigma_\infty^{(\alpha\gamma)} - 4\pi R_N^2\sigma_\infty^{(\beta\gamma)} + \Omega_\Pi \ , \\
\Delta F_S &= 4\pi R^2\sigma_\infty^{(\alpha\beta)} + 4\pi R_N'^2\sigma_\infty^{(\alpha\gamma)} + 4\pi R_N'^2\int\limits_h^\infty \Pi_D(h')\,\mathrm{d}h \\
&\quad - 4\pi R_N^2\sigma_\infty^{(\beta\gamma)} \ .
\end{aligned}
\tag{S-42}
$$

---

[5] In Eq. (S-39) the contributions to $\Delta N^{(\beta\to\alpha)}$ from the adsorption on the opposite sides of the liquid film are ignored. It is a result of the assumption that the surface tensions are replaced by constant $\sigma_\infty^{(\alpha\gamma)}$ and $\sigma_\infty^{(\beta\gamma)}$.

In Eq. (S-42), the quantity ΔF_{W} denotes the work of nucleus wetting in a thin liquid film. The quantity ΔF_{S} denotes the contribution to the formation work originating from the change in surface energy. (see also Section S.1.7).

Considering Eq. (S-13) for Π_{D} and neglecting the term $\left(p^{(\beta)} - p_\infty\right)\left(V_R - V_{R_{\mathrm{N}}}\right)$ in Eq. (S-42), the formation work reads (Shchekin et al. 2008, Eq. (30) therein):

$$
\begin{aligned}
\Delta F &= -\Delta N^{(\beta\to\alpha)}\left[\mu^{(\beta)} - \mu_\star^{(\beta\to\alpha)}\right] + \Delta N^{(\gamma\to\alpha)}\left[\mu_\star^{(\gamma\to\alpha)} - \mu_\infty^{(\gamma)}\right] \\
&\quad + 4\pi R^2 \sigma_\infty^{(\alpha\beta)} + \Delta F_{\mathrm{W}}\,, \\
\Delta F_{\mathrm{W}} &= 4\pi R_{\mathrm{N}}'^2\left[\sigma_\infty^{(\alpha\gamma)} + l^{(\star)}\Pi_{\mathrm{D}}(h)\right] - 4\pi R_{\mathrm{N}}^2\sigma_\infty^{(\beta\gamma)}\,.
\end{aligned}
$$
$$(\text{S-43})$$

The chemical potentials $\mu^{(\beta)}$, $\mu_\star^{(\beta\to\alpha)}$, $\mu_\star^{(\gamma\to\alpha)}$, and $\mu_\infty^{(\gamma)}$ are given by Eqs. (S-7), (S-16), (S-21), and (S-22), respectively.

S.1.4 Thermodynamic conditions for the equilibrium droplet

According to Eq. (S-43), the formation work is a function of two independent variables: the number of solvent molecules, $\Delta N^{(\beta\to\alpha)}$, and the number of solute molecules, $\Delta N^{(\gamma\to\alpha)}$, in the solution film. However, alternatively one can also use the radius of the solution drop, R, and the radius of the residual core, R_{N}'. The equilibrium state of the droplet is controlled by two thermodynamic conditions corresponding to the locations of the minima and saddle points of the formation work:

- the "external solvent equilibrium" between the solvent in the vapour phase β and the solvent in the liquid phase α:

$$
\left.\frac{\partial\Delta F}{\partial\Delta N^{(\beta\to\alpha)}}\right|_{\Delta N^{(\gamma\to\alpha)}} = \mu^{(\beta\to\alpha)} - \mu^{(\beta)} = 0\,, \qquad (\text{S-44})
$$

- the "internal solute equilibrium" between the solute in the residual solid phase γ' and the solute in the liquid phase α:

$$
\left.\frac{\partial\Delta F}{\partial\Delta N^{(\gamma\to\alpha)}}\right|_{\Delta N^{(\beta\to\alpha)}} = \mu^{(\gamma\to\alpha)} - \mu^{(\gamma\prime)} = 0\,. \qquad (\text{S-45})
$$

The partial derivatives of ΔF can be interpreted as the "thermodynamic driving forces" toward equilibrium. At equilibrium the driving forces vanish, i. e., external equilibrium is established when the chemical potentials of solvent molecules in the vapour and in the liquid are equal, and internal equilibrium is established when the chemical potentials of solute molecules in the liquid and in the residual core are equal, correspondingly.

In order to evaluate the equilibrium conditions given by Eqs. (S-44) and (S-45), we will derive two useful closure relations. The first one provides a constraint on the volume of the liquid film phase, $V^{(\alpha)}$. The volume of the binary solution depends on its temperature, T, pressure, $p^{(\alpha)}$, and the numbers of molecules of each component, $\Delta N^{(\beta \to \alpha)}$ and $\Delta N^{(\gamma \to \alpha)}$, i. e., $V^{(\alpha)}(T, p^{(\alpha)}, \Delta N^{(\beta \to \alpha)}, \Delta N^{(\gamma \to \alpha)})$. At constant temperature and pressure, the total differential of the solution volume upon addition or removal of either component reads:

$$
\begin{aligned}
\mathrm{d}\, V^{(\alpha)} \;=\; & \left[\frac{\partial V^{(\alpha)}}{\partial \Delta N^{(\beta \to \alpha)}} \right]_{T, p^{(\alpha)}, \Delta N^{(\gamma \to \alpha)}} \mathrm{d}\, \Delta N^{(\beta \to \alpha)} \\
& + \left[\frac{\partial V^{(\alpha)}}{\partial \Delta N^{(\gamma \to \alpha)}} \right]_{T, p^{(\alpha)}, \Delta N^{(\beta \to \alpha)}} \mathrm{d}\, \Delta N^{(\gamma \to \alpha)} \,.
\end{aligned}
\tag{S-46}
$$

The partial molar volumes of both components in the solution, i. e., the solvent and solute molecules, are defined as follows:

$$
v^{(\beta \to \alpha)} = \left[\frac{\partial V^{(\alpha)}}{\partial \Delta N^{(\beta \to \alpha)}} \right]_{\Delta N^{(\gamma \to \alpha)}} \,, \qquad v^{(\gamma \to \alpha)} = \left[\frac{\partial V^{(\alpha)}}{\partial \Delta N^{(\gamma \to \alpha)}} \right]_{\Delta N^{(\beta \to \alpha)}} \,.
\tag{S-47}
$$

The volume of the solution, $V^{(\alpha)}$, can be determined upon integration of the total differential (S-46), with consideration that $V^{(\alpha)}$ is an Eulerian function:

$$
V^{(\alpha)} = N^{(\alpha)} v^{(\alpha)} = \Delta N^{(\beta \to \alpha)} v^{(\beta \to \alpha)} + \Delta N^{(\gamma \to \alpha)} v^{(\gamma \to \alpha)} \,.
\tag{S-48}
$$

Here, $v^{(\alpha)}$ denotes the mean molecular volume of solution molecules. Rederivation of the total differential of $V^{(\alpha)}$ from Eq. (S-48) and comparison with $\mathrm{d}V^{(\alpha)}$ from Eq. (S-46) leads to the following constraint on $V^{(\alpha)}$:

$$
\boxed{\Delta N^{(\beta \to \alpha)} \, \mathrm{d}v^{(\beta \to \alpha)} + \Delta N^{(\gamma \to \alpha)} \, \mathrm{d}v^{(\gamma \to \alpha)} = 0 \,.}
\tag{S-49}
$$

The second condition is given by the Gibbs–Duhem relation and sets a constraint on the chemical potentials of solvent and solute molecules in the binary solution:

$$
S^{(\alpha)} \, \mathrm{d}T - V^{(\alpha)} \, \mathrm{d}p^{(\alpha)} + \Delta N^{(\beta \to \alpha)} \, \mathrm{d}\mu^{(\beta \to \alpha)} + \Delta N^{(\gamma \to \alpha)} \, \mathrm{d}\mu^{(\gamma \to \alpha)} = 0 \,.
\tag{S-50}
$$

The quantities $S^{(\alpha)}$ and $V^{(\alpha)}$ in Eq. (S-50) denote the entropy and volume of the binary liquid. Inserting $\mu^{(\beta \to \alpha)}$ and $\mu^{(\gamma \to \alpha)}$ from Eqs. (S-16) and (S-21) into Eq. (S-50), considering Eq. (S-49), and assuming isothermal-isobaric change of the system ($\mathrm{d}T = 0$, $\mathrm{d}p^{(\alpha)} = 0$), one arrives at the second constraint, which is known as *Duhem–Margules equation*:

$$
\boxed{\Delta N^{(\beta \to \alpha)} \, \mathrm{d}\mu_\star^{(\beta \to \alpha)} + \Delta N^{(\gamma \to \alpha)} \, \mathrm{d}\mu_\star^{(\gamma \to \alpha)} = 0 \,.}
\tag{S-51}
$$

With consideration of the constraints (S-49), (S-51) and the relations (S-34), (S-39)–(S-41), one can straightforwardly differentiate ΔF given by Eq. (S-43) with respect to $\Delta N^{(\beta \to \alpha)}$:

$$
\left. \frac{\partial \Delta F}{\partial \Delta N^{(\beta \to \alpha)}} \right|_{\Delta N^{(\gamma \to \alpha)}} = -\left[\mu^{(\beta)} - \mu_\star^{(\beta \to \alpha)} \right]
$$
$$
+ v^{(\beta \to \alpha)}(x) \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h) \right] . \tag{S-52}
$$

Comparing the right-hand side of Eq. (S-52) with the right-hand side of Eq. (S-44), one obtains a general expression for the chemical potential of solvent molecules in the solution:

$$
\begin{aligned}
\mu^{(\beta \to \alpha)} &= \mu_\star^{(\beta \to \alpha)} + v^{(\beta \to \alpha)}(x) \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h) \right] \\
&= \mu_\infty^{(\beta)} + k_B T \ln \left[\frac{a_{\text{solvent}}(x)}{a_{\text{solvent}}(0)} \right] \\
&\quad + v^{(\beta \to \alpha)}(x) \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h) \right] .
\end{aligned} \tag{S-53}
$$

In view of Eq. (S-11), Equation (S-53) coincides with Eq. (S-16).

At external equilibrium, the thermodynamic driving force for the transfer of solvent molecules from the vapour phase into the liquid phase must vanish. With consideration of the definitions for $\mu^{(\beta)}$ and $\mu_\star^{(\beta \to \alpha)}$ according to Eqs. (S-7) and (S-16), respectively, one arrives at the following *generalisation of the Gibbs–Kelvin–Köhler equation of the theory of nucleation on soluble particles* at $\mu^{(\beta \to \alpha)} = \mu^{(\beta)}$ (Shchekin et al. 2008):

$$
\begin{aligned}
\left. \mathcal{F}_{\text{GKK}} \left(S^{(\beta)}, R_N', R \right) \right|_{\substack{T=\text{const} \\ R_N=\text{const}}} &= -k_B T \ln S^{(\beta)} \\
&+ k_B T \ln \left[\frac{a_{\text{solvent}}(x(R, R_N'))}{a_{\text{solvent}}(0)} \right] \\
&+ v^{(\beta \to \alpha)}(x) \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h) \right] = 0 .
\end{aligned} \tag{S-54}
$$

At $R \to \infty$ the equilibrium condition simplifies to $S^{(\beta)} = a_{\text{solvent}}(x)$, i. e., the relative humidity equals the solvent (water) activity.

Analogously, the partial derivative of ΔF according to Eq. (S-43) with respect to $\Delta N^{(\gamma \to \alpha)}$ results in:

$$
\begin{aligned}
\left. \frac{\partial \Delta F}{\partial \Delta N^{(\gamma \to \alpha)}} \right|_{\Delta N^{(\beta \to \alpha)}} &= \mu_\star^{(\gamma \to \alpha)} - \mu_\infty^{(\gamma)} \\
&+ v^{(\gamma \to \alpha)}(x) \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h) \right] \\
&- v^{(\gamma)} \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h) + \frac{2\sigma_\infty^{(\alpha\gamma)}}{R_N'} + \left(1 + \frac{2l^{(\star)}}{R_N'} \right) \Pi_D(h) \right] .
\end{aligned}
\tag{S-55}
$$

At internal equilibrium, the thermodynamic driving force for the transfer of solute molecules from the solid phase into the liquid phase must vanish, i. e., $\mu^{(\gamma \to \alpha)} = \mu^{(\gamma\prime)}$. Setting the right-hand side of Eq. (S-55) equal to zero, one arrives at the following *generalisation of the Ostwald–Freundlich equation of the theory of solutions* (Shchekin et al. 2008):

$$
\begin{aligned}
\left. \mathcal{F}_{\mathrm{OF}} \left(R_N', R \right) \right|_{\substack{T=\mathrm{const} \\ R_N=\mathrm{const}}} &= k_B T \ln \left[\frac{a_{\mathrm{solute}}(x(R, R_N'))}{a_{\mathrm{solute}}(x_\infty)} \right] \\
&+ v^{(\gamma \to \alpha)}(x) \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h) \right] \\
&- v^{(\gamma)} \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h) \right. \\
&\left. + \frac{2\sigma_\infty^{(\alpha\gamma)}}{R_N'} + \left(1 + \frac{2l^{(\star)}}{R_N'} \right) \Pi_D(h) \right] = 0 .
\end{aligned}
\tag{S-56}
$$

The same result follows also from Eq. (S-30). Equations (S-54) and (S-56) serve as governing equations for determination of the humidity growth factor.

S.1.5 Determination of the vapour condensation growth factor

To determine the dependence of the droplet radius R on the vapour saturation ratio $S^{(\beta)}$ at equilibrium between the droplet and the ambient vapour one has to distinguish the following cases:

1. **Case 1: Partial dissolution of the initial core in the solution film.** This case corresponds to the existence of an equilibrium residual core. Replacing R_N' in the Gibbs–Kelvin–Köhler Eq. (S-54) (subscript GKK) by the relation

17

$R'_N(R)$ from the Ostwald–Freundlich Eq. (S-56) (subscript OF), one obtains a relation for the determination of $R(S^{(\beta)})$:

$$\mathcal{F}_{\text{GKK}}\left(S^{(\beta)}, R'_N, R\right)\Big|_{\substack{T=\text{const}\\R_N=\text{const}}} = 0$$

$$+\mathcal{F}_{\text{OF}}\left(R'_N, R\right)\Big|_{\substack{T=\text{const}\\R_N=\text{const}}} = 0 \qquad (\text{S-57})$$

$$\rightsquigarrow \mathcal{F}_{\text{GKK+OF}}\left(S^{(\beta)}, R\right)\Big|_{\substack{T=\text{const}\\R_N=\text{const}}} = 0\ .$$

For fixed values of temperature T and initial core radius R_N the droplet radius R can be numerically determined as a function of the vapour saturation ratio $S^{(\beta)}$ by finding the root of the transcendental equation $\mathcal{F}_{\text{GKK+OF}}\left(S^{(\beta)}, R\right) = 0$ in Eq. (S-57), which yields the relation $R = f_1(T, R_N, S^{(\beta)})$.

2. **Case 2: Complete dissolution of the initial core in the solution film.** In this case one has $R'_N = 0$ (or $N^{(\gamma)} = 0$) and the second term on the right-hand side of Eq. (S-54) containing the relative solute concentration x is retained, but the fourth term containing the disjoining pressure vanishes. Therewith the Gibbs–Kelvin–Köhler Eq. (S-54) reduces to:

$$\mathcal{F}_{\text{GKK}}\left(S^{(\beta)}, R\right)\Big|_{\substack{T=\text{const}\\R_N=\text{const}}} = 0\ . \qquad (\text{S-58})$$

The solution of Eq. (S-58) provides the relation $R = f_2(T, R_N, S^{(\beta)})$.

3. **Case 3: Insolubility of the substrate core.** In this case one has $R'_N = R_N$ (or $N^{(\gamma)} = N_0^{(\gamma)}$ and $x = 0$) and the second term on the right-hand side of Eq. (S-54) containing the relative solute concentration vanishes, but the fourth term containing the disjoining pressure is retained ($\Pi_D \neq 0$). Therewith the Gibbs–Kelvin–Köhler Eq. (S-54) reduces to:

$$\mathcal{F}_{\text{GKK}}\left(S^{(\beta)}, R\right)\Big|_{\substack{T=\text{const}\\R_N=\text{const}}} = 0\ . \qquad (\text{S-59})$$

The solution of Eq. (S-59) provides the relation $R = f_3(T, R_N, S^{(\beta)})$.

A further possibility is the case that the core is a mixture of soluble and insoluble species, but such a scenario will not be considered here. Knowing the relation $R(T, R_N, S^{(\beta)})$, the measurable vapour condensation growth factor GF can be directly determined:

$$\text{GF} = \frac{R}{R_N} = R_N^{-1} f_i(T, R_N, S^{(\beta)})\ , \quad i = 1, \ldots, 3\ . \qquad (\text{S-60})$$

S.1.6 Determination of the deliquescence humidity

The deliquescence barrier determines the thermodynamic condition for the prompt transition from the equilibrium state with the partially dissolved residual core to the equilibrium state with the completely dissolved residual core ("deliquescence transition") (cf. Fig. 1, middle and right picture). The existence of an equilibrium aerosol state with a partially dissolved condensation nucleus requires the coeval fulfilment of both external and internal equilibrium conditions (cf. Eqs. (S-44) and (S-45)).

The generalised Ostwald–Freundlich Eq. (S-56) allows the determination of the number of solvent molecules in the film, $\Delta N^{(\beta \to \alpha)}$, as a function of the number of solute molecules in the film, $\Delta N^{(\gamma \to \alpha)}$ (or as a function of the number of solute molecules in the residual core, $N^{(\gamma)} = N_0^{(\gamma)} - \Delta N^{(\gamma \to \alpha)}$), at which the residual core is in thermodynamic equilibrium with the enveloping solution film. The function $\Delta N^{(\beta \to \alpha)}(N^{(\gamma)})$ has a maximum, denoted by $\Delta N_i^{(\beta \to \alpha)}$, above which the condition for the internal equilibrium (S-56) is not satisfied any longer and the residual core will inevitably disappear. Thus, the maximum value $\Delta N_i^{(\beta \to \alpha)}$ sets an upper limit for the number of solvent molecules, at which the internal equilibrium with a residual core is established at a specified initial core radius R_N and temperature T. The analysis of Eq. (S-57) at fixed $S^{(\beta)}$ and R_N reveals the existence of a maximum of the right-hand side of Eq. (S-54) at certain threshold value $\Delta N_{th}^{(\beta \to \alpha)} < \Delta N_i^{(\beta \to \alpha)}$. This value establishes a threshold value $S_{th}^{(\beta)}$ in such a way that there is no solution of Eq. (S-54) at $S^{(\beta)} > S_{th}^{(\beta)}$. Starting from this threshold prompt barrierless transition to the state with complete dissolution of the residual core sets in.

Let us write for convenience the chemical potentials of the solvent molecules in the vapour and liquid phases, respectively, in thermal units $k_B T$:

$$b^{(\beta)} = \frac{\mu^{(\beta)} - \mu_\infty^{(\beta)}}{k_B T} = \ln S^{(\beta)} , \quad b^{(\beta \to \alpha)} = \frac{\mu^{(\beta \to \alpha)} - \mu_\infty^{(\beta)}}{k_B T} . \qquad \text{(S-61)}$$

By virtue of Eq. (S-53), one gets for chemical potential of the solvent molecules in the liquid film in thermal units:

$$
\begin{aligned}
b^{(\beta \to \alpha)}(R, R_N') = & \ln \left[\frac{a_{solvent}(x(R, R_N'))}{a_{solvent}(0)} \right] \\
& + \frac{v^{(\beta \to \alpha)}(x(R, R_N'))}{k_B T} \left[\frac{2\sigma_\infty^{(\alpha\beta)}}{R} - \left(\frac{R_N'}{R} \right)^2 \Pi_D(h(R, R_N')) \right] .
\end{aligned}
\qquad \text{(S-62)}
$$

The deliquescence threshold (and the corresponding deliquescence vapour saturation ratio $S_{th}^{(\beta)}$ and deliquescence relative humidity DRH) is equal to $b^{(\beta \to \alpha)}$

according to Eq. (S-62) evaluated at $\Delta N_{\text{th}}^{(\beta \to \alpha)}$:

$$
\begin{aligned}
b_{\text{th}}^{(\beta)} &= b^{(\beta \to \alpha)}\big|_{\Delta N_{\text{th}}^{(\beta \to \alpha)}} \;, \\
S_{\text{th}}^{(\beta)} &= \exp\left(b_{\text{th}}^{(\beta)}\right) \;, \quad \text{DRH} = 100\% \times S_{\text{th}}^{(\beta)} \;.
\end{aligned}
\tag{S-63}
$$

The determination of $b_{\text{th}}^{(\beta)}$ proceeds as follows:

1. Firstly, the drop radius is determined as a function of residual radius, $R = R(R'_{\text{N}})$, from the numerical solution of the transcendental OF equation (S-56).

2. Secondly, the function $R'_{\text{N}} = R'_{\text{N}}(R)$ is inserted into Eq. (S-62), delivering the solvent chemical potential as a function of drop radius, $b^{(\beta \to \alpha)} = b^{(\beta \to \alpha)}(R)$.

3. Thirdly, from $b^{(\beta \to \alpha)} = b^{(\beta \to \alpha)}(R)$ the maximum value $b_{\text{th}}^{(\beta \to \alpha)}$ is determined, which is equal to the deliquescence vapour saturation ratio according to Eq. (S-63).

Finally, it should be said that fast deliquescence transition occurs at slightly smaller values of vapour saturation ratio $S^{(\beta)}$ than $S_{\text{th}}^{(\beta)}$. As shown by Shchekin et al. (2013), these smaller values can be found within kinetic theory of two-dimensional nucleation over the saddle point of the work of droplet formation.

S.1.7 Addendum: Comments on the mechanical and thermodynamic concept of disjoining pressure

The surface tension of the flat interface separating two adjacent bulk phases α and β reads (Krotov and Rusanov 1999, Eq. (1.16) therein):

$$
\sigma_{\infty}^{(\alpha\beta)} = \int_{-\infty}^{\infty} (p_{\text{N}} - p_{\text{T}}) \; \mathrm{d}z \;.
\tag{S-64}
$$

Here, p_{N} denotes the normal pressure across a flat interface between the adjacent bulk phases (equal to the normal component of the pressure tensor), and p_{T} denotes the tangential component of the pressure tensor. The z-axis is orientated in normal direction to the interface. At the interface the following condition is fulfilled:

$$
\frac{\partial p_{\text{N}}}{\partial z} = 0 \;, \quad p_{\text{N}} = p^{(\alpha)} = p^{(\beta)} \;.
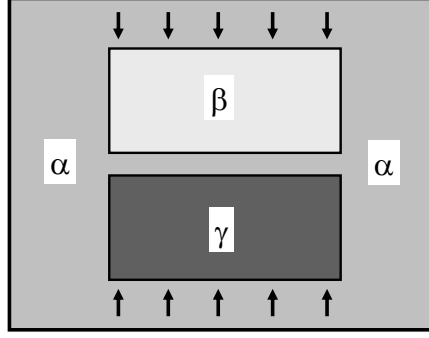\tag{S-65}
$$

Figure 2: Three-phases system consisting of a flat film of phase α with thickness h, which is positioned between two adjacent bulk phases γ and β. Redrawn from Krotov and Rusanov (1999, p. 26, Fig. 1.2 therein).

For a three-phases system consisting of an asymmetric, flat film of phase α with thickness h, which is positioned between two adjacent bulk phases β and γ according to Fig. 2, the mechanical equilibrium condition in the absence of an external field reads:

$$\frac{\partial p_\mathrm{N}}{\partial z} = 0 \,, \quad p_\mathrm{N} = p^{(\gamma)} = p^{(\beta)} \,. \tag{S-66}$$

Inserting Eq. (S-66) into Eq. (S-64), the film tension σ^film reads:

$$
\begin{aligned}
\sigma^\mathrm{film} &= \int_{-\infty}^{\infty} (p_\mathrm{N} - p_\mathrm{T}) \, \mathrm{d}z \\
&= \int_{-\infty}^{\infty} \left(p^{(\gamma)} - p_\mathrm{T}\right) \mathrm{d}z = \int_{-\infty}^{\infty} \left(p^{(\beta)} - p_\mathrm{T}\right) \mathrm{d}z \,.
\end{aligned}
\tag{S-67}
$$

Now, we consider a thin film, inside which there is no bulk phase. The transition from a thick film to a thin one occurs, when the surface layers of the thick film begin to overlap. For a thin film $p^{(\alpha)}$ is not equal to the pressures $p^{(\gamma)}$ and $p^{(\beta)}$. The pressure difference

$$
\begin{aligned}
\Pi_\mathrm{D} &\equiv p^{(\beta)} - p^{(\alpha)} = p^{(\gamma)} - p^{(\alpha)} \,, \\
\Pi_\mathrm{D} &\equiv p_\mathrm{N} - p^{(\alpha)} \,,
\end{aligned}
\tag{S-68}
$$

is called *"disjoining pressure"* (Derjaguin 1955, Derjaguin et al. 1987, Rusanov 1978, pp. 279-285 therein, Krotov and Rusanov 1999, pp. 24-31, Fig. 1.2 therein, Rusanov and Shchekin 2005). The disjoining pressure can be interpreted as follows: To squeeze a film to thickness h, an excess pressure $\Pi_\mathrm{D}(h)$ must be applied to offset the tendency of the film phase to separate or to "disjoin" the confining

phases. If $\Pi_D{>}0$, the film is wetting, and if $\Pi_D{<}0$, it is non-wetting (i. e., the film wants to retreat from the region between the confining phases) (Davis 1996, pp. 370-371 therein). The disjoining pressure obeys the following boundary conditions:

$$\lim_{h\to\infty} \Pi_D(h) = 0 \ , \quad \lim_{h\to\infty} [\Pi_D(h) \cdot h] = 0 \ , \tag{S-69}$$

In the limiting case of an infinitely thick film, the disjoining pressure vanishes.

The definition of the film tension in Eq. (S-67) corresponds to the choice of a single dividing surface. Using two dividing surfaces, we can define the surface tensions of a thin film (only taken together) as follows:

$$
\begin{aligned}
\sigma^{(\alpha\gamma)} + \sigma^{(\alpha\beta)} &= \int\limits_{-\infty}^{-h/2} \left(p^{(\gamma)} - p_T\right) \, \mathrm{d}z + \int\limits_{-h/2}^{h/2} \left(p^{(\alpha)} - p_T\right) \, \mathrm{d}z \\
&+ \int\limits_{h/2}^{\infty} \left(p^{(\beta)} - p_T\right) \, \mathrm{d}z \ .
\end{aligned}
\tag{S-70}
$$

Inserting Eq. (S-68) into Eq. (S-70) and considering Eq. (S-67), we obtain:

$$\sigma^{\mathrm{film}} = \sigma^{(\alpha\gamma)} + \sigma^{(\alpha\beta)} + \Pi_D h \ . \tag{S-71}$$

From a rigorous thermodynamic approach, Krotov and Rusanov (1999, pp. 27-29, Eq. (1.108) therein) derived:

$$\left(\frac{\mathrm{d}\sigma^{\mathrm{film}}}{\mathrm{d}\Pi_D}\right)_T \approx h \ . \tag{S-72}$$

The integration of Eq. (S-72) from $\Pi_D{=}0$ to $\Pi_D(h)$ results in:

$$\sigma^{\mathrm{film}} \left(\Pi_D(h)\right) \approx \sigma^{\mathrm{film}} \left(\Pi_D{=}0\right) + \int\limits_0^{\Pi_D(h)} h \, \mathrm{d}\Pi_D(h) \ . \tag{S-73}$$

The term $\sigma^{\mathrm{film}} \left(\Pi_D{=}0\right)$ is the film tension in the limiting case of a thick film, given by the sum of the bulk surface tensions from both sides of the film:

$$\sigma^{\mathrm{film}} \left(\Pi_D{=}0\right) = \sigma_\infty^{(\alpha\gamma)} + \sigma_\infty^{(\alpha\beta)} \ . \tag{S-74}$$

Therewith we obtain (Krotov and Rusanov 1999, Eq. (1.109) therein):

$$
\begin{aligned}
\sigma^{\mathrm{film}} &= \sigma_\infty^{(\alpha\gamma)} + \sigma_\infty^{(\alpha\beta)} + \Delta\sigma_\Pi \ , \\
\Delta\sigma_\Pi &= \int\limits_0^{\Pi_D(h)} h \, \mathrm{d}\Pi_D(h) \ .
\end{aligned}
\tag{S-75}
$$

Partial integration of Eq. (S-75) with consideration of the boundary conditions Eq. (S-69) yields (Krotov and Rusanov 1999, Eq. (1.110) therein):

$$\sigma^{\text{film}} = \sigma_\infty^{(\alpha\gamma)} + \sigma_\infty^{(\alpha\beta)} + \Pi_{\text{D}}h + \int\limits_h^\infty \Pi_{\text{D}}(h)\,\mathrm{d}h \ . \tag{S-76}$$

Comparing Eq. (S-71) with Eq. (S-76), we obtain the relation between film and bulk properties of the surface tensions of a flat thin film (Krotov and Rusanov 1999, Eq. (1.111) therein)):

$$
\begin{aligned}
\sigma^{(\alpha\gamma)} + \sigma^{(\alpha\beta)} &\approx \sigma_\infty^{(\alpha\gamma)} + \sigma_\infty^{(\alpha\beta)} + I \ , \\
I &= \int\limits_h^\infty \Pi_{\text{D}}(h)\,\mathrm{d}h \ .
\end{aligned}
\tag{S-77}
$$

In order to derive an approximative expression for the term ΔF_{S} in Eq. (S-42), we consider a curved thin film, which is bounded by two interfaces: the (inner) liquid/solid interface $(\alpha\gamma)$ with radius R_{N}' and surface area $A_{R_{\text{N}}'}{=}4\pi R_{\text{N}}'^2$, and the (outer) liquid/vapour interface $(\alpha\beta)$ with radius $R{=}R_{\text{N}}'{+}h$ and surface area $A_R{=}4\pi R^2$. The surface are of the initial core is given by $A_{R_{\text{N}}}{=}4\pi R_{\text{N}}^2$. The quantity ΔF_{S} reads:

$$
\begin{aligned}
\Delta F_{\text{S}} &= A_{R_{\text{N}}'}\sigma^{(\alpha\gamma)} + A_R\sigma^{(\alpha\beta)} - A_{R_{\text{N}}}\sigma_\infty^{(\beta\gamma)} \\
&= A_{R_{\text{N}}'}\left(\sigma^{(\alpha\gamma)} + \sigma^{(\alpha\beta)}\right)\left[1 + \left(\frac{A_R - A_{R_{\text{N}}'}}{A_{R_{\text{N}}'}}\right)\frac{\sigma^{(\alpha\beta)}}{\sigma^{(\alpha\gamma)} + \sigma^{(\alpha\beta)}}\right] \\
&\quad - A_{R_{\text{N}}}\sigma_\infty^{(\beta\gamma)} \ .
\end{aligned}
\tag{S-78}
$$

Restricting our consideration to droplet sizes, for which the capillary approximation of the droplet is valid, one has $\sigma^{(\alpha\beta)}{=}\sigma_\infty^{(\alpha\beta)}$. Inserting Eq. (S-77) into Eq. (S-78) with the same accuracy, we obtain the final expression for ΔF_{S}:

$$
\begin{aligned}
\Delta F_{\text{S}} &= 4\pi R_{\text{N}}'^2\sigma_\infty^{(\alpha\gamma)} + 4\pi R^2\sigma_\infty^{(\alpha\beta)} + 4\pi R_{\text{N}}'^2\int\limits_h^\infty \Pi_{\text{D}}(h)\,\mathrm{d}h \\
&\quad - 4\pi R_{\text{N}}^2\sigma_\infty^{(\beta\gamma)} \ .
\end{aligned}
\tag{S-79}
$$

The general case of arbitrarily and non-uniformly curved interfaces and thin films has been considered by Rusanov and Shchekin (2005). The authors proposed a general thermodynamic theory, which is based on the evaluation of the total non-diagonal pressure tensor with consideration of external fields.

S.2 Efflorescence behaviour from classical nucleation theory (CNT)

S.2.1 Basic scenario and assumptions

The prompt transition from a homogeneous solution droplet to a heterogeneous solution droplet with a stable crystal core is called efflorescence transition. It performs via homogeneous crystallisation, i. e., precipitation of solute crystals from a supersaturated solution droplet. Supersaturation of the solution can be achieved by decreasing the chemical potential of the solvent vapour (e. g., by decreasing the temperature). Here, efflorescence is assumed to be the result of only one successful crystallisation event inside the solution droplet. This assumption implies that the growth rate of a single supercritical solute crystal is very large at the solution supersaturation, where homogeneous crystallisation takes place. This condition enables the first supercritical crystal germ formed to grow quickly enough to aggregate a stable equilibrium core inside the droplet before any other supercritical crystal germ is formed. Additionally, it can be assumed that the primary germ formation is favoured over the secondary one due to the latent heat release during germ growth, which immediately raises the temperature of the solution in the droplet. This reduces the solution supersaturation and, consequently, the rate of homogeneous crystallisation to a very small value. Apart from that it should be noted that we consider here homogeneous nucleation in very small volume (like in molecular dynamics cell). In such an environment the formation of a single supercritical embryo is sufficient to decrease the supersaturation of the droplet solution.

S.2.2 Efflorescence humidity

Employing the classical nucleation theory (CNT), the efflorescence condition reads (e. g., Gao et al. 2007, Onasch et al. 2000, Pant et al. 2006, Parsons et al. 2006):

$$J_{\mathrm{hom}}\Big|_{\mathrm{effl}} = \frac{1}{V_R(R_{\mathrm{effl}})\,\tau_{\mathrm{ind}}} \;, \quad V_R(R_{\mathrm{effl}}) = \frac{4\pi}{3}R_{\mathrm{effl}}^3 \;. \qquad \text{(S-80)}$$

Here, J_{hom} denotes the rate of homogeneous crystallisation, R_{effl} the radius of the solution droplet at the onset of efflorescence, respectively, and τ_{ind} the induction time, defined as the time the system spent at constant droplet composition prior to

nucleation[6]. The rate of homogeneous crystallisation is obtained from CNT:

$$
\begin{aligned}
J_{\mathrm{hom}} &= J_{\mathrm{hom},0} \exp\left(-\frac{\Delta F_{\mathrm{c}}}{k_{\mathrm{B}} T}\right) , \\[2mm]
J_{\mathrm{hom},0} &= \rho^{(\gamma)} \left(\frac{k_{\mathrm{B}} T}{h}\right) \exp\left(-\frac{\Delta F_{\mathrm{act}}}{k_{\mathrm{B}} T}\right) , \quad \rho^{(\gamma)} = \frac{1}{v^{(\gamma)}} , \\[2mm]
\frac{\Delta F_{\mathrm{c}}}{k_{\mathrm{B}} T} &= \frac{16\pi}{3} \frac{\left[\sigma_\infty^{(\alpha\gamma)}\right]^3 \left[v^{(\gamma)}\right]^2}{(k_{\mathrm{B}} T)^3 \left(\ln S^{(\alpha)}\right)^2} , \quad S^{(\alpha)} = \frac{a_{\mathrm{solute}}(x)}{a_{\mathrm{solute}}(x_\infty)} .
\end{aligned}
\tag{S-81}
$$

Here, $J_{\mathrm{hom},0}$ denotes the kinetic prefactor of the homogeneous nucleation rate, the term $\Delta F_{\mathrm{c}}/(k_{\mathrm{B}} T)$ the free energy in thermal units required to form a critical embryo of the new phase (crystal) from its mother phase (solution), $\rho^{(\gamma)}$ is the molecular concentration of the solute in the crystalline nucleus in units of m^{-3} (with $v^{(\gamma)}$ the already introduced molecular volume of the substrate matter). The terms $k_{\mathrm{B}} T/h$ and $\Delta F_{\mathrm{act}}/(k_{\mathrm{B}} T)$ are the frequency and free energy barrier (in thermal units) of a solute molecule to jump from the solution to the crystalline nucleus, respectively. The critical formation work is a nonlinear function of the solution saturation ratio $S^{(\alpha)}$, which is the ratio of the actual solute activity to the solute activity at solubility of the substrate matter. Combining Eqs. (S-80) and (S-81), one obtains a transcendental equation for the determination of the relative solute concentration at the efflorescence transition, x_{effl}:

$$
\mathcal{F}_{\mathrm{CNT}}\big(R(x_{\mathrm{effl}})\big)\Big|_{\substack{T = \mathrm{const} \\ R_{\mathrm{N}} = \mathrm{const} \\ R'_{\mathrm{N}}}}
\tag{S-82}
$$

$$
= \left\{ \frac{16\pi}{3} \left[\frac{\sigma_\infty^{(\alpha\gamma)}}{k_{\mathrm{B}} T}\right]^3 \frac{\left[v^{(\gamma)}\right]^2}{\ln\left[\frac{4}{3}\pi [R(x_{\mathrm{effl}})]^3 J_{\mathrm{hom},0}\, \tau_{\mathrm{ind}}\right]} \right\}^{1/2} - \ln\left[\frac{a_{\mathrm{solute}}(x_{\mathrm{effl}})}{a_{\mathrm{solute}}(x_\infty)}\right] = 0 .
$$

To find the root of Eq. (S-82), i. e., the droplet radius at the onset of efflorescence, one has to consider a closure condition to determine the relative solute concentration as a function of the initial and residual core radii and the droplet radius. The closure condition given by the composition–geometry relation $x = x(R_{\mathrm{N}}, R'_{\mathrm{N}}, R)$ (written as an implicit equation $\mathcal{F}_{\mathrm{comp-geom}}(x, R_{\mathrm{N}}, R'_{\mathrm{N}}, R)=0$), which will be derived in Section S.3.3.

With consideration of this relation, one can determine x_{effl} and R_{effl} from the transcendental Eq. (S-82). For known R_{effl}, the efflorescence humidity,

$$
\mathrm{ERH} = 100\% \times S_{\mathrm{effl}}^{(\beta)} ,
$$

---

[6] The time τ_{ind} can be considered as the latency time required for the appearance of a super-critical embryo.

is the root of the relation $R = f_2(T, R_N, S^{(\beta)})$ according to the second-case GKK equation (S-58). The system of equations that have to be solved can be summarised as follows:

$$
\begin{aligned}
\mathcal{F}_{\mathrm{CNT}} + \mathcal{F}_{\mathrm{comp-geom}} &\rightsquigarrow \mathcal{F}_{\mathrm{CNT+(comp-geom)}}(x_{\mathrm{effl}}) = 0 \\
\mathcal{F}_{\mathrm{comp-geom}} &\rightsquigarrow R_{\mathrm{effl}} = R_{\mathrm{effl}}(x_{\mathrm{effl}}) \\
\mathcal{F}_{\mathrm{GKK}} + \mathcal{F}_{\mathrm{comp-geom}} &\rightsquigarrow R_{\mathrm{effl}} = f_2(T, R_N, S^{(\beta)}_{\mathrm{effl}}) \\
\hline
\rightsquigarrow \quad S^{(\beta)}_{\mathrm{effl}} &= S^{(\beta)}_{\mathrm{effl}}(T, R_N) \, .
\end{aligned}
\tag{S-83}
$$

S.3 Thermophysical parameters for the aqueous sodium-chloride solution

S.3.1 Solvent and solute activities

The activities are determined separately for the high-molality regime, $m \geq m_0 = 10 \, \mathrm{mol\,kg^{-1}}$, and the low-molality regime, $m < m_0$.

(a) Highly concentrated solutions

Following Gao et al. (2007), for application in the high-molality regime, we employ the Ally–Braunstein statistical mechanics theory of multilayer adsorption of water on sodium-chloride particles in concentrated solutions to determine the solvent and solute activities (Ally and Braunstein 1998, Eqs. (35) and (36) therein):

$$
a_{\mathrm{solvent}} = \frac{H - X}{H} \, , \quad a_{\mathrm{solute}} = \left(\frac{rA - X}{rA} \right)^r \, .
\tag{S-84}
$$

Here, $H = \Delta N^{(\beta \to \alpha)}$ denotes the number of solvent (water) molecules in the solution, $A = \Delta N^{(\gamma \to \alpha)}$ the number of solute molecules in the solution, and X is the (so far unknown) number of particles of water partaking in monolayer adsorption on solute particles. The exponent r is the number of adsorption sites offered per particle of solute. The theory predicts the following condition for the determination of X (Ally and Braunstein 1998, Eq. (10) therein):

$$
\frac{X^2}{(rA - X)(H - X)} = \exp \left(-\frac{\Delta U_A}{k_B T} \right) = c_A \, .
\tag{S-85}
$$

The property $\Delta U_A = U_A - U_1$ is the change of internal energy due to monolayer adsorption with $U_A < 0$ denoting the internal energy of monolayer adsorption of water onto solute particles and $U_1 < 0$ the internal energy of liquefaction of pure

water. Because of $|U_A|>|U_1|$, one has $\Delta U_A<0$ for monolayer adsorption and $\Delta U_A=0$ for adsorption of water beyond the first layer. For aqueous $NaCl$ solution, Ally et al. (2001) derived the following experimental parameters: $r=2.845$ and $c_A=3.813$.

Equation (S-85) has two solutions:

$$X_{\pm} = \frac{c_A(rA+H)}{2(c_A-1)} \pm \sqrt{\left[\frac{c_A(rA+H)}{2(c_A-1)}\right]^2 - \frac{c_A rAH}{c_A-1}} \ . \qquad \text{(S-86)}$$

Here, only the solution X_- is physically reasonable.

Using normalised properties,

$$\widetilde{H} = \frac{\Delta N^{(\beta\to\alpha)}}{\Delta N^{(\beta\to\alpha)}} = 1 \ , \quad \widetilde{A} = \frac{\Delta N^{(\gamma\to\alpha)}}{\Delta N^{(\beta\to\alpha)}} = M_W m \ , \quad \widetilde{X}(m) = \frac{X}{\Delta N^{(\beta\to\alpha)}} \ ,$$

the solvent and solute activities can be expressed in terms of molality (see Fig. 3):

$$
\begin{aligned}
a_{\text{solvent}}(m) &= 1 - \widetilde{X}(m) \ , \\
a_{\text{solute}}(m) &= \left(\frac{rM_W m - \widetilde{X}(m)}{rM_W m}\right)^r \ , \\
\widetilde{X}(m) &= \frac{c_A(rM_W m+1)}{2(c_A-1)} - \sqrt{\left[\frac{c_A(rM_W m+1)}{2(c_A-1)}\right]^2 - \frac{c_A rM_W m}{c_A-1}} \ , \\
m &\geq m_0 \ .
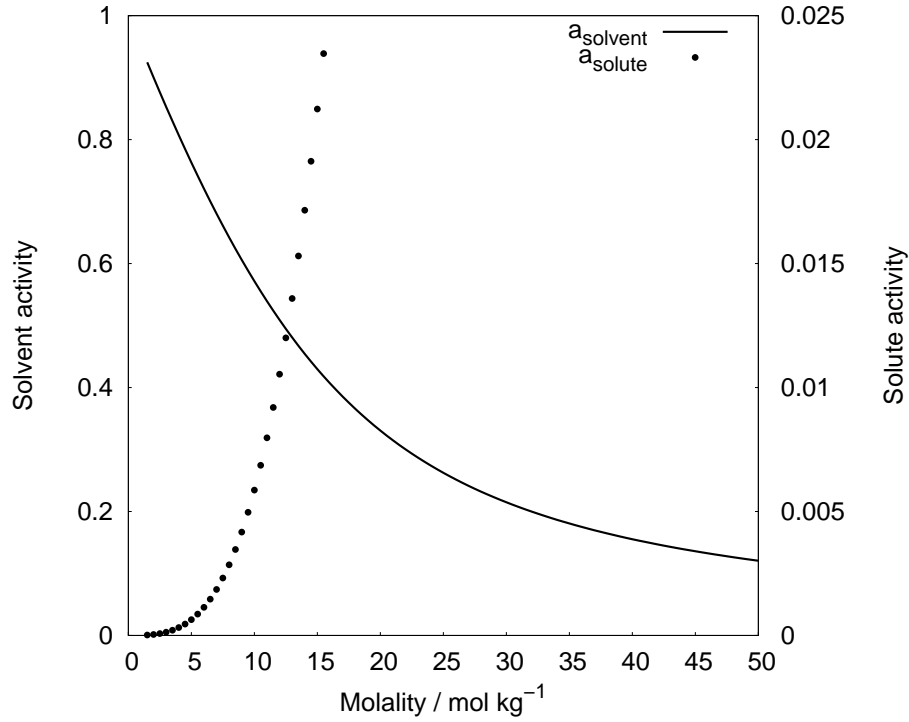\end{aligned}
$$

$$\text{(S-87)}$$

Figure 3: Solvent and solute activities for highly concentrated solutions at T=298 K according to Eq. (S-87).

(b) Moderately concentrated and diluted solutions

For application in the range $m < m_0$ we use the solvent (water) activity, $a_{\text{solvent}} = a_{\text{W}}$, proposed by Tang et al. (1986) for T=298 K in the form given by Gao et al. (2007, Eq. (12) therein):

$$
\begin{aligned}
a_{\text{W}} = \exp\Bigg[& -0.03604\,m + 0.01649 \times (1 + 1.37\sqrt{m}) \\
& -0.01649 \times 4.60517 \times \log_{10}(1 + 1.37\sqrt{m}) \\
& -\frac{0.01649}{1 + 1.37\sqrt{m}} - 1.1601 \times 10^{-3}m^2 - 2.6572 \times 10^{-4}m^3 \\
& +1.7029 \times 10^{-5}m^4 \Bigg] .
\end{aligned}
\tag{S-88}
$$

For more convenient use, Eq. (S-88) has been refitted with high accuracy to the

following polynomial (see Fig. 4):

$$\ln[a_{\text{solvent}}(m)] = \sum_{k=1}^{4} c_k m^k ,$$

$$c_1 = -3.22382 \times 10^{-2} , \quad c_2 = -1.24185 \times 10^{-3} ,$$

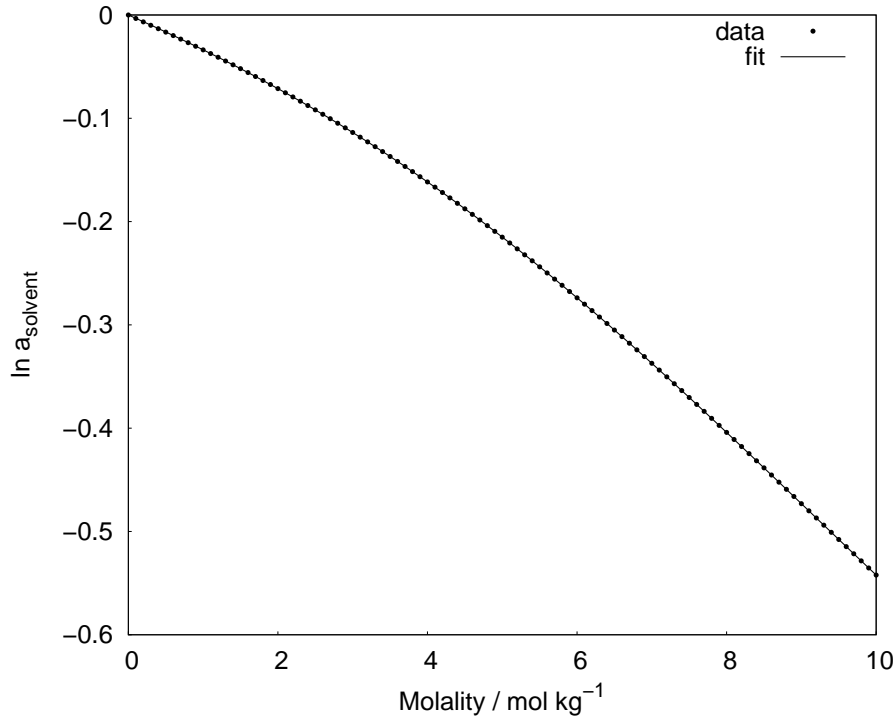$$c_3 = -2.69339 \times 10^{-4} , \quad c_4 = 1.73745 \times 10^{-5} .$$

(S-89)

Figure 4: Refitted water activity of Tang et al. (1986) at $T=298\,\text{K}$ according to Eq. (S-89).

The solute activity for $m < m_0$ is obtained from integration of the Duhem–Margules equation (S-51), written as:

$$\boxed{d\left[\ln a_{\text{solvent}}(m)\right] + m M_{\text{W}}\, d\left[\ln a_{\text{solute}}(m)\right] = 0 .}$$

(S-90)

$$\ln[a_{\text{solute}}(m)] = \ln[a_{\text{solute}}(m_0)] - \frac{1}{M_{\text{W}}} \int_{m_0}^{m} \left(\frac{1}{\widetilde{m}} \frac{d\ln[a_{\text{solvent}}(\widetilde{m})]}{d\widetilde{m}} \right) d\widetilde{m} .$$

(S-91)

By virtue of Eq. (S-89) one gets:

$$
\begin{aligned}
\ln[a_{\text{solute}}(m)] &= \ln[a_{\text{solute}}(m_0)] - \frac{I(m_0, m)}{M_{\text{W}}} , \\
I(m_0, m) &= c_1 \ln\left(\frac{m}{m_0}\right) + 2c_2(m - m_0) \\
&\quad + \frac{3}{2}c_3(m^2 - m_0^2) + \frac{4}{3}c_4(m^3 - m_0^3) , \\
m &< m_0 .
\end{aligned}
\tag{S-92}
$$

The value of the solute activity $a_{\text{solute}}(m_0)$ is obtained from Ally–Braunstein theory.

(c) Polynom representation in the whole range

For use in the whole range $m \leq 50 \, \text{mol} \, \text{kg}^{-1}$ the following fit functions have been derived (see Fig. 5):

$$
\begin{aligned}
\ln[a_{\text{solvent}}(m)] &= \sum_{k=1}^{5} c_k' m^k , \\
c_1' &= -0.0307631 , \quad c_2' = -0.00387181 , \\
c_3' &= 0.000197245 , \quad c_4' = -3.84431 \times 10^{-6} , \\
c_5' &= 2.71606 \times 10^{-8} ,
\end{aligned}
\tag{S-93}
$$

$$
\begin{aligned}
\ln[a_{\text{solute}}(m)] &= c_1'' \ln(m) + c_2'' m^{0.1} + c_3'' \sqrt{m} + \sum_{k=4}^{7} c_3'' m^{k-3} , \\
c_1'' &= 2.73246 , \quad c_2'' = -11.674 , \\
c_3'' &= -0.44687 , \quad c_4'' = 0.656717 , \\
c_5'' &= -0.023862 , \quad c_6'' = 0.000435512 , \\
c_7'' &= -3.06136 \times 10^{-6} .
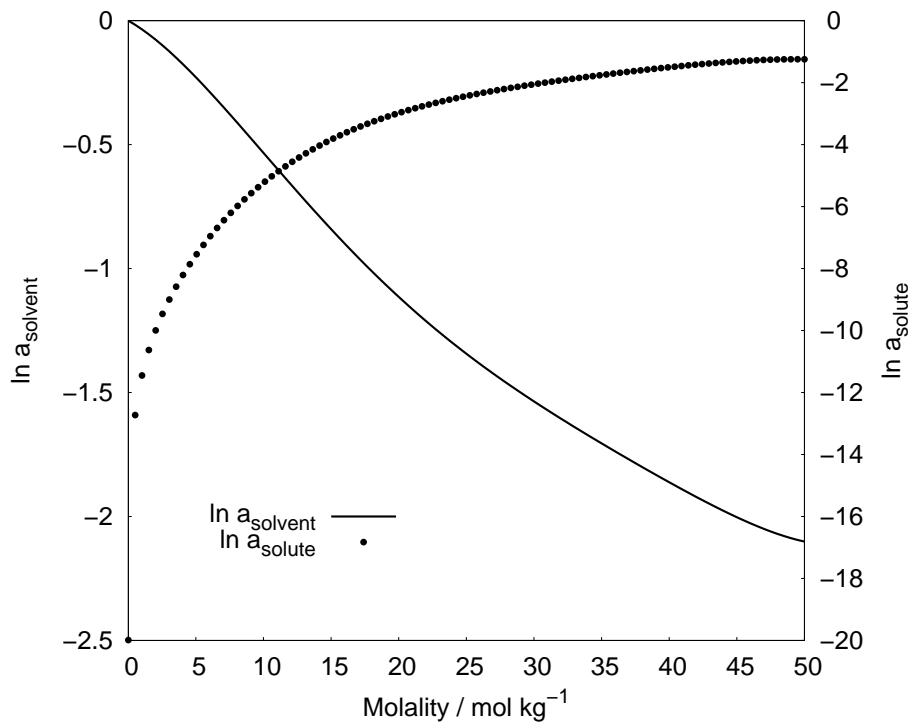\end{aligned}
\tag{S-94}
$$

Figure 5: Solvent and solute activities for the whole range at $T{=}298\,\mathrm{K}$ according to Eqs. (S-93) and (S-94).

S.3.2 Partial molecular volumes

Our three-phases system is specified as follows: the solvent phase β refers to water vapour (H_2O), the solute phase γ to sodium chloride ($NaCl$), and the solution phase α is an aqueous salt solution consisting of condensed H_2O and dissolved $NaCl$. The following considerations are based on the empirical finding, that the molecular volumes of solvent and solute molecules will change upon mixing of their respective pure phases to form a solution. The numbers of the solvent and

solute molecules in the liquid film obey the following relations:

$$
\begin{aligned}
N^{(\alpha)} &= \Delta N^{(\beta \to \alpha)} + \Delta N^{(\gamma \to \alpha)} \ , \\
m^{(\alpha)} &= N^{(\alpha)} M^{(\alpha)} = \Delta N^{(\beta \to \alpha)} M^{(\beta)} + \Delta N^{(\gamma \to \alpha)} M^{(\gamma)} \ , \\
V^{(\alpha)} &= N^{(\alpha)} v^{(\alpha)} = \Delta N^{(\beta \to \alpha)} v^{(\beta \to \alpha)} + \Delta N^{(\gamma \to \alpha)} v^{(\gamma \to \alpha)} \ , \\
x &= \frac{\Delta N^{(\gamma \to \alpha)}}{\Delta N^{(\alpha)}} = \frac{M^{(\beta)} m}{1 + M^{(\beta)} m} \ , \\
x_{\mathrm{m}} &= \frac{\Delta N^{(\gamma \to \alpha)} M^{(\gamma)}}{N^{(\alpha)} M^{(\alpha)}} = \frac{M^{(\gamma)} m}{1 + M^{(\gamma)} m} \ .
\end{aligned}
\tag{S-95}
$$

Here, x and x_{m} are the molar and mass fractions, respectively, of the solute in the solution, $m^{(\alpha)}$ and $V^{(\alpha)}$ are the mass and volume of the solution, respectively. The molar masses of the aqueous solution, the solvent, and the solute, $M^{(\alpha)}$, $M^{(\beta)}$, and $M^{(\gamma)}$, respectively, read:

$$
\begin{aligned}
M^{(\alpha)} &= (1-x) M^{(\beta)} + x M^{(\gamma)} \ , \\
M^{(\beta)} &= 18.01528 \times 10^{-3} \, \mathrm{kg \, mol^{-1}} \ , \\
M^{(\gamma)} &= 58.44 \times 10^{-3} \, \mathrm{kg \, mol^{-1}} \ .
\end{aligned}
\tag{S-96}
$$

The apparent partial volume of the solute molecule in the solution, $v_{\star}^{(\gamma \to \alpha)}$, is defined as follows:

$$
V^{(\alpha)} = \Delta N^{(\beta \to \alpha)} v_0^{(\beta \to \alpha)} + \Delta N^{(\gamma \to \alpha)} v_{\star}^{(\gamma \to \alpha)} \ .
\tag{S-97}
$$

Here, $v_0^{(\beta \to \alpha)}$ is the partial molecular volume of the pure solvent particles (pure liquid water corresponding to $x=0$). The volume of the solution can also be expressed by the following relation:

$$
V^{(\alpha)} = \frac{m^{(\alpha)}}{\varrho^{(\alpha)}} \ , \qquad m^{(\alpha)} = \frac{\Delta N^{(\beta \to \alpha)} M^{(\beta)} + \Delta N^{(\gamma \to \alpha)} M^{(\gamma)}}{N_{\mathrm{A}}} \ .
\tag{S-98}
$$

In Eq. (S-98), $\varrho^{(\alpha)}$ denotes the mass density of the aqueous solution. For aqueous sodium-chloride solution, a parameterisation of Hämeri et al. (2001, Table 1 therein)[7] is used:

$$
\begin{aligned}
\varrho^{(\alpha)}(T, x_{\mathrm{m}}) &= \varrho_0^{(\beta \to \alpha)}(T) \left(1 + \varepsilon_1 x_{\mathrm{m}} + \varepsilon_2 x_{\mathrm{m}}^2 \right) \ , \\
\varepsilon_1 &= 6.9707 \times 10^{-1} \ , \quad \varepsilon_2 = 2.58987 \times 10^{-1} \ .
\end{aligned}
\tag{S-99}
$$

---

[7]Note, that the unit conversion factor is missing in the solution density expression given by Hämeri et al. (2001, Table 1 therein). For convenience, here the mass density is rewritten in a slightly different form compared to the original paper.

Here, $\varrho_0^{(\beta\to\alpha)}$ denotes the mass density of pure liquid water. To consider the temperature dependence of $\varrho_0^{(\beta\to\alpha)}$, here we have replaced the value of $\varrho_0^{(\beta\to\alpha)} = 998.45\,\mathrm{kg\,m^{-3}}$, used in the original formulation, with the mass density of pure liquid water proposed by Pruppacher and Klett (1997, p. 87, Eq. (3-13) therein):

$$
\begin{aligned}
\frac{\varrho_0^{(\beta\to\alpha)}(T)}{\mathrm{kg\,m^{-3}}} &= \frac{\displaystyle\sum_{k=0}^{5} a_k\,(T-273.15)^k}{1+b(T-273.15)} \ , \\
a_0 &= 999.8396\ , \quad a_1 = 18.224944\ , \\
a_2 &= -7.922210\times10^{-3}\ , \quad a_3 = -55.44846\times10^{-6}\ , \\
a_4 &= 149.7562\times10^{-9}\ , \quad a_5 = -393.2952\times10^{-12}\ , \\
b &= 18.159725\times10^{-3}\ .
\end{aligned}
\tag{S-100}
$$

The partial molecular volume of the pure solvent in the liquid phase, $v_0^{(\beta\to\alpha)}$, is given by the following relation:

$$
v_0^{(\beta\to\alpha)} = \frac{M^{(\beta)}}{N_A\varrho_0^{(\beta\to\alpha)}} \ .
\tag{S-101}
$$

The partial molecular volumes $v^{(\beta\to\alpha)}$, $v^{(\gamma\to\alpha)}$, and $v_\star^{(\gamma\to\alpha)}$ are obtained from rearrangement of the expressions for $V^{(\alpha)}$ given by Eqs. (S-95) and (S-97):

$$
v^{(\beta\to\alpha)} = \frac{V^{(\alpha)} - \Delta N^{(\gamma\to\alpha)} v^{(\gamma\to\alpha)}}{\Delta N^{(\beta\to\alpha)}} \ ,
\tag{S-102}
$$

$$
v^{(\gamma\to\alpha)} = \frac{V^{(\alpha)} - \Delta N^{(\beta\to\alpha)} v^{(\beta\to\alpha)}}{\Delta N^{(\gamma\to\alpha)}} \ ,
\tag{S-103}
$$

$$
v_\star^{(\gamma\to\alpha)} = \frac{V^{(\alpha)} - \Delta N^{(\beta\to\alpha)} v_0^{(\beta\to\alpha)}}{\Delta N^{(\gamma\to\alpha)}} \ .
\tag{S-104}
$$

Inserting $V^{(\alpha)}$ from Eq. (S-98) into the right-hand side of Eq. (S-104), one arrives at the conditional equation for the calculation of $v_\star^{(\gamma\to\alpha)}$ as a function of solute mass fraction:

$$
v_\star^{(\gamma\to\alpha)}(x_m) = \frac{M^{(\gamma)}}{N_A\varrho^{(\alpha)}(x_m)}\left\{1 + \frac{1-x_m}{x_m}\left(1 - \frac{\varrho^{(\alpha)}(x_m)}{\varrho_0^{(\beta\to\alpha)}}\right)\right\} \ .
\tag{S-105}
$$

The partial molecular volume $v^{(\gamma\to\alpha)}$ is obtained from partial differentiation of Eq. (S-97) with respect to $\Delta N^{(\gamma\to\alpha)}$ at $\Delta N^{(\beta\to\alpha)}=$const. :

$$
\begin{aligned}
v^{(\gamma\to\alpha)} &= \left[\frac{\partial V^{(\alpha)}}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} \\
&= v_\star^{(\gamma\to\alpha)} + \Delta N^{(\gamma\to\alpha)} \left[\frac{\partial v_\star^{(\gamma\to\alpha)}}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} .
\end{aligned}
\tag{S-106}
$$

Inserting $v^{(\gamma\to\alpha)}$ from Eq. (S-106) into the the right-hand side of Eq. (S-102) and considering Eq. (S-97), one obtains:

$$
v^{(\beta\to\alpha)} = v_0^{(\beta\to\alpha)} - \frac{\left[\Delta N^{(\gamma\to\alpha)}\right]^2}{\Delta N^{(\beta\to\alpha)}} \left[\frac{\partial v_\star^{(\gamma\to\alpha)}}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} .
\tag{S-107}
$$

In order to expand Eq. (S-107), we will employ the following auxiliary relations:

- From the definition of molality:

$$
\Delta N^{(\beta\to\alpha)} = \frac{N_A m_0^{(\beta\to\alpha)}}{M^{(\beta)}} , \quad \Delta N^{(\gamma\to\alpha)} = N_A m_0^{(\beta\to\alpha)} m .
\tag{S-108}
$$

Here, $m_0^{(\beta\to\alpha)}$ denotes an arbitrary reference value of the solvent mass in the solution[8].

- From partial derivation of $v_\star^{(\gamma\to\alpha)}$ according to Eq. (S-104):

$$
\left[\frac{\partial v_\star^{(\gamma\to\alpha)}}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} = \frac{1}{\Delta N^{(\gamma\to\alpha)}} \left\{ \left[\frac{\partial V^{(\alpha)}}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} - v_\star^{(\gamma\to\alpha)} \right\} .
\tag{S-109}
$$

- From partial derivation of $V^{(\alpha)}$ according to Eq. (S-98):

$$
\left[\frac{\partial V^{(\alpha)}}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} = \frac{M^{(\gamma)}}{N_A \varrho^{(\alpha)}} - \frac{V^{(\alpha)}}{\varrho^{(\alpha)}} \left[\frac{\partial \varrho^{(\alpha)}}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} .
\tag{S-110}
$$

- From partial derivation of $\varrho^{(\alpha)}$ according to Eq. (S-99):

$$
\left[\frac{\partial \varrho^{(\alpha)}}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} = \varrho_0^{(\beta\to\alpha)} \left(\varepsilon_1 + 2\varepsilon_2 x_m\right) \left[\frac{\partial x_m}{\partial \Delta N^{(\gamma\to\alpha)}}\right]_{\Delta N^{(\beta\to\alpha)}} .
\tag{S-111}
$$

---

[8]We will see, that the final expressions do not depend on $m_0^{(\beta\to\alpha)}$.

- From partial derivation of the x_m and m according to Eq. (S-95):

$$\left[\frac{\partial x_\mathrm{m}}{\partial \Delta N^{(\gamma \to \alpha)}}\right]_{\Delta N^{(\beta \to \alpha)}} = \frac{x_\mathrm{m}}{m}(1 - x_\mathrm{m})\left[\frac{\partial m}{\partial \Delta N^{(\gamma \to \alpha)}}\right]_{\Delta N^{(\beta \to \alpha)}} ,$$

$$\left[\frac{\partial m}{\partial \Delta N^{(\gamma \to \alpha)}}\right]_{\Delta N^{(\beta \to \alpha)}} = \frac{1}{N_\mathrm{A} m_0^{(\beta \to \alpha)}} .$$

(S-112)

Inserting these auxiliary expressions successively into Eq. (S-107), one arrives after rearrangement at the following final expression for the determination of $v^{(\beta \to \alpha)}$ as a function of solute mass fraction:

$$v^{(\beta \to \alpha)}(x_\mathrm{m}) = \frac{M^{(\beta)}}{N_\mathrm{A} \varrho^{(\alpha)}(x_\mathrm{m})}\left[1 + \left(\frac{\varrho_0^{(\beta \to \alpha)}}{\varrho^{(\alpha)}(x_\mathrm{m})}\right) f(x_\mathrm{m})\right] ,$$

$$f(x_\mathrm{m}) = \varepsilon_1 \left(\frac{x_\mathrm{m}}{1 - x_\mathrm{m}}\right) + (2\varepsilon_2 - \varepsilon_1)\left(\frac{x_\mathrm{m}^2}{1 - x_\mathrm{m}}\right)$$

$$- 2\varepsilon_2 \left(\frac{x_\mathrm{m}^3}{1 - x_\mathrm{m}}\right) .$$

(S-113)

The partial molecular volume $v^{(\gamma \to \alpha)}$ can be determined either from Eq. (S-106) or, by virtue of Eq. (S-113), directly from Eq. (S-103). Inserting $V^{(\alpha)}$ from Eq. (S-98) into the right-hand side of Eq. (S-103), on arrives after rearrangement at the following final expression for the determination of $v^{(\gamma \to \alpha)}$ as a function of solute mass fraction:

$$v^{(\gamma \to \alpha)}(x_\mathrm{m}) = \frac{M^{(\gamma)}}{N_\mathrm{A} \varrho^{(\alpha)}(x_\mathrm{m})}\left\{1 + \frac{1 - x_\mathrm{m}}{x_\mathrm{m}}\left(1 - \frac{\varrho^{(\alpha)}(x_\mathrm{m})}{\varrho^{(\beta \to \alpha)}(x_\mathrm{m})}\right)\right\} ,$$

$$\varrho^{(\beta \to \alpha)}(x_\mathrm{m}) = \frac{M^{(\beta)}}{N_\mathrm{A} v^{(\beta \to \alpha)}(x_\mathrm{m})} .$$

(S-114)

Here, $\varrho^{(\beta \to \alpha)}$ denotes the mass density of the solvent in the solution. The partial molecular volume of the solution particles reads:

$$v^{(\alpha)} = \frac{M^{(\alpha)}}{N_\mathrm{A} \varrho^{(\alpha)}} .$$

(S-115)

Finally, the partial molecular volume of pure solute particles, $v^{(\gamma)}$, can be determined from the mass density of the solute, $\varrho^{(\gamma)}$:

$$v^{(\gamma)} = \frac{M^{(\gamma)}}{N_\mathrm{A} \varrho^{(\gamma)}} , \quad \varrho^{(\gamma)} = 2.165 \times 10^3 \,\mathrm{kg\,m}^{-3} .$$

(S-116)

With Eqs. (S-113)– (S-116) we have the sought-after conditional equations for determination of the partial molecular volumes $v^{(\beta \to \alpha)}$, $v^{(\gamma \to \alpha)}$, and $v^{(\gamma)}$ as function of the chemical composition of the heterogeneous droplet, x (see Fig. 6).
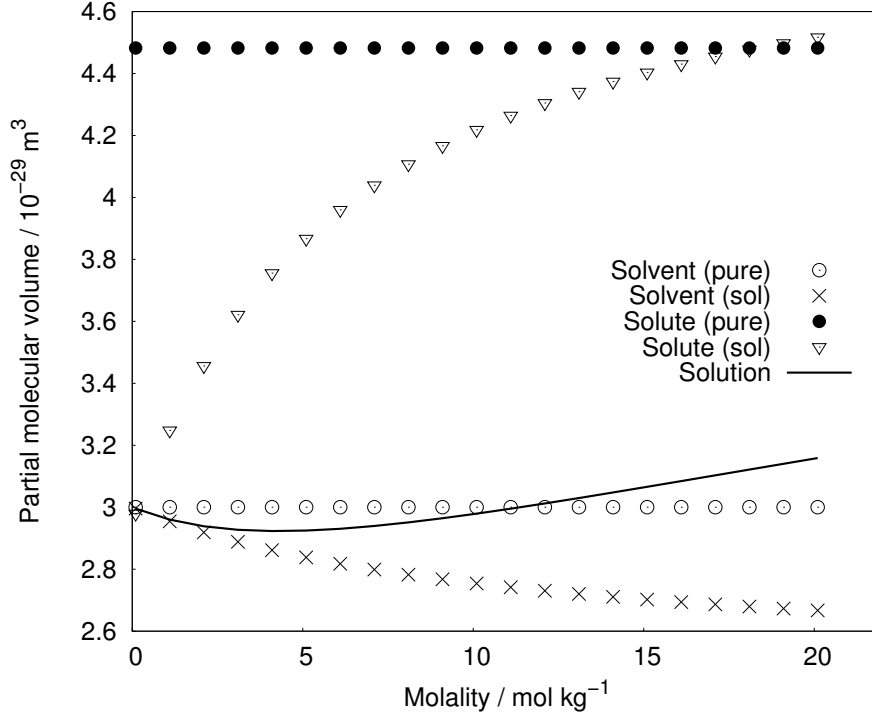

Figure 6: Partial molecular volumes of the pure solvent $\left(v_0^{(\beta \to \alpha)}\right)$, the solvent in the solution $\left(v^{(\beta \to \alpha)}\right)$, the pure solute $\left(v^{(\gamma)}\right)$, the solute in the solution $\left(v^{(\gamma \to \alpha)}\right)$, and the solution $\left(v^{(\alpha)}\right)$ as function of the chemical composition of the heterogeneous droplet x according to Eqs. (S-101) and (S-113)– (S-116) at $T{=}298\,\text{K}$.

S.3.3   Composition–geometry relation

Combining Eqs. (S-34), (S-39), and (S-41), one arrives at:

$$x = \cfrac{1}{1 + \cfrac{v^{(\gamma \to \alpha)}}{v^{(\beta \to \alpha)}} \left[\left(\cfrac{V_R - V_{R'_N}}{V_{R_N} - V_{R'_N}} \right) \cfrac{v^{(\gamma)}}{v^{(\gamma \to \alpha)}} - 1 \right]} \tag{S-117}$$

On the other hand, from Eq. (S-95) one obtains the following relation between mole and mass fraction of solute, $x = x(x_{\mathrm{m}})$:

$$x = \frac{M^{(\beta)} x_{\mathrm{m}}}{M^{(\gamma)} - \left[M^{(\gamma)} - M^{(\beta)} \right] x_{\mathrm{m}}} \ . \tag{S-118}$$

Equating Eqs. (S-117) and (S-118) results in a conditional equation for the determination of x_{m} as function of $V_{R_{\mathrm{N}}}$, $V_{R'_{\mathrm{N}}}$, and V_R:

$$\frac{M^{(\beta)} x_{\mathrm{m}}}{M^{(\gamma)} - \left[M^{(\gamma)} - M^{(\beta)} \right] x_{\mathrm{m}}} = \frac{1}{1 + \dfrac{v^{(\gamma \to \alpha)}}{v^{(\beta \to \alpha)}} \left[\left(\dfrac{V_R - V_{R'_{\mathrm{N}}}}{V_{R_{\mathrm{N}}} - V_{R'_{\mathrm{N}}}} \right) \dfrac{v^{(\gamma)}}{v^{(\gamma \to \alpha)}} - 1 \right]} \ . \tag{S-119}$$

After rearrangement of Eq. (S-119), one obtains the following transcendental equation for the determination of x_{m} at $V_{R_{\mathrm{N}}} \neq V_{R'_{\mathrm{N}}}$:

$$\boxed{\begin{aligned} \mathcal{F}_{\mathrm{comp-geom}}\left(x_{\mathrm{m}}, V_{R_{\mathrm{N}}}, V_{R'_{\mathrm{N}}}, V_R\right) &= \frac{V_{R_{\mathrm{N}}} - V_{R'_{\mathrm{N}}}}{V_R - V_{R'_{\mathrm{N}}}} \\ &- \frac{M^{(\beta)} v^{(\gamma)} x_{\mathrm{m}}}{M^{(\beta)} v^{(\gamma \to \alpha)}(x_{\mathrm{m}}) x_{\mathrm{m}} + M^{(\gamma)} v^{(\beta \to \alpha)}(x_{\mathrm{m}}) (1 - x_{\mathrm{m}})} = 0 \ . \end{aligned}} \tag{S-120}$$

At $V_{R_{\mathrm{N}}} = V_{R'_{\mathrm{N}}} = V_R$ one has $x_{\mathrm{m}} = 0$.

S.3.4 Solubility of sodium chloride

The solubility of NaCl solute, s_∞, is the ratio of mole number of solute to mole number of solvent at equilibrium with the flat interface between the solid and solution (Seinfeld and Pandis 2006, p. 453, Table 10.2):

$$\begin{aligned} s_\infty &= \left(\frac{\Delta N^{(\gamma \to \alpha)}}{\Delta N^{(\beta \to \alpha)}} \right)_\infty = A + BT + CT^2 \ , \\ A &= 0.1805 \ , \quad B = -5.310 \times 10^{-4} \ , \quad C = 9.965 \times 10^{-7} \ , \\ x_\infty &= \frac{s_\infty}{s_\infty + 1} \ , \quad m_\infty = \frac{s_\infty}{M_{\mathrm{W}}} \ . \end{aligned} \tag{S-121}$$

S.3.5 Activation energy for liquid/solid interface-crossing diffusion

Owing to lack of direct measurements of the activation energy, ΔF_{act}, appearing in the expression for the homogeneous crystallisation rate, Eq. (S-81), here we

employ a relation between the viscosity and a characteristic activation energy ΔE_η as proposed by Glasstone et al. (1941) (see also Jeffery and Austin 1997):

$$\eta = \eta_0 \exp\left(\frac{\Delta E_\eta}{k_B T}\right) \,, \tag{S-122}$$

Assuming $\Delta F_{act} \approx \Delta E_\eta$ and neglecting the temperature dependence of the prefactor η_0, one arrives at the following expression:

$$\frac{d\ln(\eta/T)}{d(1/T)} = \frac{\Delta E_\eta}{k_B}\left(1 + \frac{k_B T}{\Delta E_\eta} - \frac{T}{\Delta E_\eta}\frac{d\Delta E_\eta}{dT}\right) \,. \tag{S-123}$$

We interpret ΔE_η as a characteristic microscopic energy scale, which weakly depends on temperature in a linear way with a proportionality constant in the order of k_B, i. e., $\Delta E_\eta = k_B T + \text{const.}$. Therewith one arrives at the following approximation for ΔF_{act}:

$$\Delta F_{act} \approx k_B \frac{d\ln(\eta/T)}{d(1/T)} = k_B T\left(1 - \frac{T}{\eta}\frac{d\eta}{dT}\right) \,. \tag{S-124}$$

Equation (S-124) is known as Frenkel–Eyring equation.

Based on a critical evaluation of available data, Ozbek et al. (1977, Eq. (11) therein) recommended the following parameterisation of the viscosity (in units of centipoise, $1\,\text{cp} = 10^{-3}\,\text{Pa}\,\text{s}$) of aqueous sodium-chloride solution, $\eta^{(\alpha)}$, as function of temperature, ϑ in $^\circ$C, and molality, m:

$$
\begin{aligned}
\eta^{(\alpha)}/\text{cp} &= c_1 + c_2\exp(\alpha_1\vartheta/^\circ\text{C}) + c_3\exp(\alpha_2 m) \\
&\quad + c_4\exp\left\{\alpha_3\left[0.01(\vartheta/^\circ\text{C}) + m\right]\right\} \\
&\quad + c_5\exp\left\{\alpha_4\left[0.01(\vartheta/^\circ\text{C}) - m\right]\right\} \,, \\
c_1 &= 0.1256735 \,, \quad c_2 = 1.265347 \,, \quad c_3 = -1.105369 \,, \\
c_4 &= 0.2044679 \,, \quad c_5 = 1.308779 \,, \\
\alpha_1 &= -0.0429618 \,, \quad \alpha_2 = 0.3710073 \,, \\
\alpha_3 &= 0.4230889 \,, \quad \alpha_4 = -0.3259828 \,, \\
p &\leq 30\,\text{MPa} \,, \quad 0\,^\circ\text{C} \leq \vartheta \leq 150\,^\circ\text{C} \,, \quad m \leq 6\,\text{mol}\,\text{kg}^{-1} \,.
\end{aligned}
\tag{S-125}
$$

Owing to lack of other data we have extended the application range of the $\eta^{(\alpha)}$ formulation in the present approach until $m_{max} = 10\,\text{mol}\,\text{kg}^{-1}$, which is beyond its definition range. For higher molalities we took the $\eta^{(\alpha)}$ values at m_{max}. The molality-dependence of the activation energy according to Eq. (S-124) and of the viscosity according Eq. (S-125) are depicted in Fig. 7 for temperature of $T = 298\,\text{K}$.
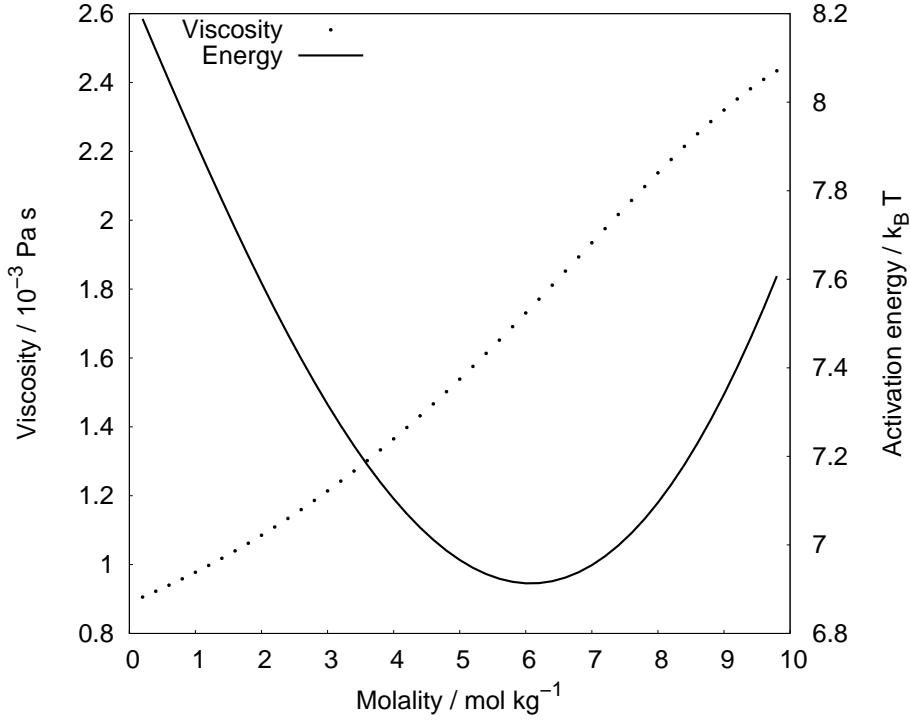
Figure 7: Activation energy according to Eq. (S-124) and viscosity according Eq. (S-125) as function of molality m at $T{=}298$ K.

S.3.6 Interfacial energies

1. For the surface tension of an aqueous NaCl solution, Russell and Ming (2002) communicated a value of $\sigma_\infty^{(\alpha\beta)}{=}(0.083{\pm}0.002)$ J m^{-2}. This value is approximately the same as the molality-dependent surface tension $\sigma_\infty^{(\alpha\beta)}(m)$ given in Pruppacher and Klett (1997, Fig. 5.2 therein) at $m{\approx}6$ mol kg^{-1}, which corresponds to the solubility of NaCl in water at room temperature (see Section S.3.4).

2. The quantity $\sigma_\infty^{(\alpha\gamma)}$ is a key quantity of the present approach, which enters the calculus via the nonequilibrium spreading coefficient s and the critical cluster formation work in the nucleation rate expression. Based on different sources, Russell and Ming (2002, see references therein) quantified the liquid/solid interfacial energy to be $\sigma_\infty^{(\alpha\gamma)}{=}(0.029 \pm 0.020)$ J m^{-2}. However, Gao et al. (2007) found a considerably larger value of $\sigma_\infty^{(\alpha\gamma)}{\approx}0.0895$ J m^{-2}. Hence, the value of $\sigma_\infty^{(\alpha\gamma)}$ is highly uncertain and varies over one order of

magnitude.

3. According to Li (2009) there is a great lack of quantitative insight into the properties of NaCl surfaces such as the interfacial energy. The reason for this is, as the author argued, the difficulties in applying widely employed methods of surface science such as scanning tunneling microscopy (STM), LEED, and photoelectron spectroscopies to the surfaces of wide band-gap ionic materials, such as NaCl in a non-destructive manner. The conventional application of these electron-based methods to insulators can lead to unwanted collateral effects such as surface charging, electron-stimulated dissociation of the alkali halides, and alkali enrichment of the selvedge, which will hamper the characterisation of the surface (Li 2009, p. 33, see references therein). For the vapour/solid interfacial energy, Russell and Ming (2002, see references therein) communicated and used a value of $\sigma_\infty^{(\beta\gamma)}$=0.213 J m^{-2}. However, with reference to different measurements the authors pointed out the large uncertainty of $\sigma_\infty^{(\beta\gamma)}$, varying in the range $(0.1-0.27)$ J m^{-2}. Similarly, citing different sources of experimental data Li (2009, see p. 38 therein) communicated a range of $\sigma_\infty^{(\beta\gamma)} = (11-24)$ meV Å^{-2} (which corresponds by virtue of $1\,\text{meV}=1.60217656\times10^{-22}$ J to $(0.176-0.385)$ J m^{-2}) for the NaCl(001) crystal[9]. Li (2009) employed density-functional theory (DFT) within the plane-wave pseudopotential approach to determine the interface energy of NaCl(001). The author found (i) an extreme insensitivity of $\sigma_\infty^{(\beta\gamma)}$ to the number of NaCl layers (slap layers) used in the calculation, (ii) a noticeable and significant impact of the choice of exchange-correlation functional upon $\sigma_\infty^{(\beta\gamma)}$ (Li 2009, see Fig. 3.1 therein and Fig. 8 here). Using three different exchange-correlation functionals and performing a qualitative judgement on the base on experience from simulations of other materials, the author suggested the best estimate of the surface energy of NaCl(001) lying in the range $\sigma_\infty^{(\beta\gamma)}$=(9−15) meV Å^{-2} (corresponding to $(0.144-0.24)$ J m^{-2}). However, Li emphasised that in the absence of reliable experimental measurements of the surface energy of NaCl(001) it is difficult to decide which functional yields the most reliable value of the interface energy. The author further concluded that "an improved estimate of the surface energy of NaCl(001) must await either new experiments or more potent calculations than those provided in the current work, both of which are now clearly needed" (Li 2009, see p. 43 therein).

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[9]The annotation corresponds to Miller indexing for crystallographic axes of a cubic (or isometric) crystal. See for example `http://en.wikipedia.org/wiki/Miller_index`, visited on May 25, 2014.
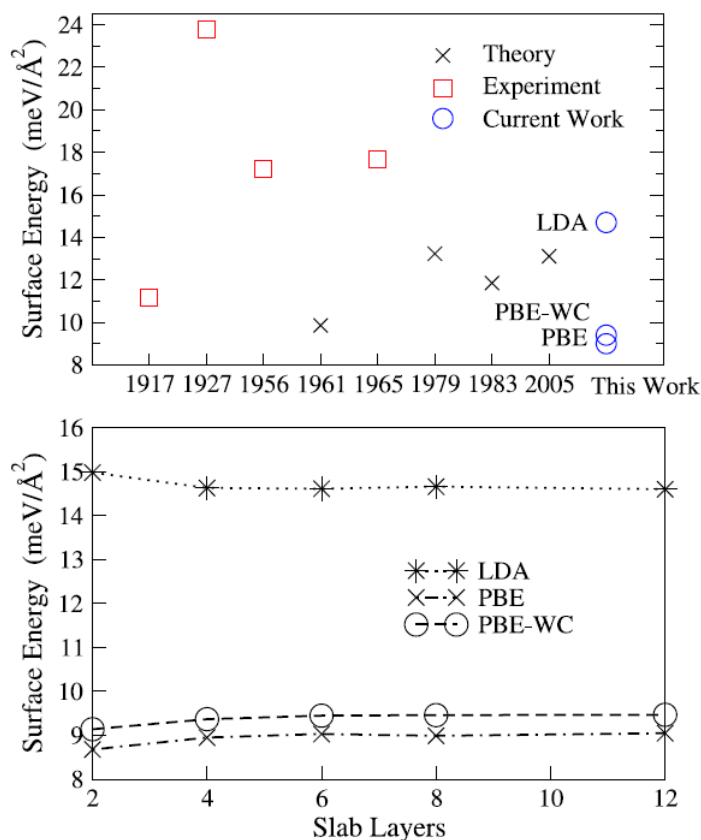
Figure 8: Top: Measured and computed values of the surface energy of NaCl(001) since 1917, together with the DFT-based values obtained by Li (2009, 'Current Work') using three different exchange-correlation functionals (LDA, PBE-WC, PBE). The references to the previously reported values from theory and experiment are given in Li (2009). Bottom: Dependence of the computed surface energy of NaCl(001) on the number of NaCl layers and exchange-correlation functional used. Abbreviations: DFT := density functional theory; LDA := local density approximation; GGA/PBE := generalised gradient approximation of Perdew, Burke and Wang (1992); GGA/PBE-WC := GGA/PBE method modified by Wuh and Cohen (2006). Taken from Li (2009, Fig. 3.1 therein).

S.3.7 Disjoining pressure parameters

A key quantity entering the exponential disjoining pressure approximation (S-13) and affecting the surface tension of a thin film is the correlation length $l^{(\star)}$. The value of $l^{(\star)}$ is in the order of the intermolecular distance in the solution, but its true physical dependence on measureable quantities is unknown so far and cannot

41

be obtained from classical heterogeneous nucleation theory. For the correlation length appearing in the expression of the disjoining pressure Marčelja and Radić (1976) proposed a value of $l^{(\star)}=3\times10^{-10}\,\mathrm{m}$.

Employing nonlocal DFT on the basis of the weighted-density approximation, both Bykov and Zeng (2002, subscript BZ) and Napari and Laaksonen (2003, subscript NL) studied the functional form of $\Pi_\mathrm{D}(h)$, and confirmed the applicability of the exponential approximation of $\Pi_\mathrm{D}(h)$ to thin liquid films. Napari and Laaksonen (2003) also studied the curvature dependence and found that both parameters, $K^{(\star)}$ and $l^{(\star)}$ decrease with the core radius. Napari and Laaksonen (2003) emphasised that the behaviour of the disjoining pressure in real fluid systems can be expected to follow DFT-based predictions. However, a parameterised equation for $\Pi_\mathrm{D}(h)$ would require knowledge of the molecular-level interactions in each particular system.

Table 1 shows the scaled values of the characteristic disjoining pressure $K^{(\star)}$ and the correlation length $l^{(\star)}$ of Bykov and Zeng (2002) and Napari and Laaksonen (2003) using the following scaling properties:

Bykov/Zeng :
$$
\begin{aligned}
\widehat{K}_\mathrm{BZ}^{(\star)} &= \frac{k_\mathrm{B}T}{\pi D_\mathrm{HS}^3/6}\ , \quad \widehat{l}_\mathrm{BZ}^{(\star)}=\widehat{z}_0=D_\mathrm{HS}\ , \\[6pt]
D_\mathrm{HS} &= f_\mathrm{D}(T^\star)\sigma_\mathrm{LJ}\ , \quad f_\mathrm{D}(T^\star)=\frac{a_1T^\star+b}{a_2T^\star+a_3}\ , \\[6pt]
T^\star &= k_\mathrm{B}T/\epsilon_\mathrm{LJ}\ , \\[4pt]
a_1 &= 0.56165\ , \quad a_2=0.60899\ , \\[4pt]
a_3 &= 0.92868\ , \quad b=0.9718\ ,
\end{aligned}
\tag{S-126}
$$

Napari/Laaksonen :
$$
\widehat{K}_\mathrm{NL}^{(\star)} = \epsilon_\mathrm{LJ}/\sigma_\mathrm{LJ}^3\ , \quad \widehat{l}_\mathrm{NL}^{(\star)}=\sigma_\mathrm{LJ}\ ,
$$

Here, z_0 denotes the location of zero film thickness $h=z-z_0=0$, D_HS the temperature-dependent hard-sphere diameter of the underlying model fluid, determined according to the Lu-Evans-Telo da Gama mapping scheme (Lu et al. 1985; Zeng and Oxtoby 1991), and $T^\star$ the scaled temperature. The quantities σ_LJ and ϵ_LJ represent the characteristic length and energy parameters of the Lennard–Jones (12-6) potential. The constants a_1, a_2, and a_3 were obtained by fitting of the Barker-Henderson hard-sphere diameter, and b was chosen to fit Monte Carlo simulations for low-temperature coexisting liquid densities (Zeng and Oxtoby 1991,

see references therein). The relations between the scaling properties read:

$$\widehat{K}_{BZ}^{(\star)}/\widehat{K}_{NL}^{(\star)} = \frac{6T^\star}{\pi f_D^3} \approx \begin{cases} 1.33 \text{ for } T^\star = 0.7 , \\ 1.71 \text{ for } T^\star = 0.9 , \end{cases}$$

$$\widehat{l}_{BZ}^{(\star)}/\widehat{l}_{NL}^{(\star)} = f_D(T^\star) \approx 1 . \tag{S-127}$$

Table 1: Scaled values of the characteristic disjoining pressure and film correlation length according to Bykov and Zeng (2002) and Napari and Laaksonen (2003).

$T^\star$	Bykov/Zeng			Napari/Laaksonen			
	$K^{(\star)}/\widehat{K}_{BZ}^{(\star)}$	$l^{(\star)}/\widehat{l}_{BZ}^{(\star)}$	$z_0/\widehat{z}_0$	$K^{(\star)}/\widehat{K}_{NL}^{(\star)}$		$l^{(\star)}/\widehat{l}_{NL}^{(\star)}$	
				planar	curved	planar	curved
0.7	0.76	1.6	2.35	0.83	0.18	1.5	0.9
0.9	0.32	1.7	3.06	–	–	–	–

Table 2 shows the absolute values of the disjoining pressure parameters for specific parameters of the Lennard-Jones potential. As reference values for the evaluation of Table 1, the Lennard-Jones parameters for argon (Ar) and water (H_2O) (Reid et al. 1988, p. 733) have been used:

$$\sigma_{LJ}^{(Ar)} = 3.542 \,\text{Å} , \quad \epsilon_{LJ}^{(Ar)}/k_B = 93.3 \text{ K} ,$$

$$\sigma_{LJ}^{(H_2O)} = 2.641 \,\text{Å} , \quad \epsilon_{LJ}^{(H_2O)}/k_B = 809.1 \text{ K} .$$

Table 2: Absolute values of the characteristic disjoining pressure and film correlation length corresponding to Table 1.

T/K	Bykov/Zeng			Napari/Laaksonen			
	$K^{(\star)}/\text{MPa}$	$l^{(\star)}/\text{Å}$	$z_0/\text{Å}$	$K^{(\star)}/\text{MPa}$		$l^{(\star)}/\text{Å}$	
				planar	curved	planar	curved
			Argon				
65	28.8	5.4	8.4	24	5.2	5.3	3.2
84	15.9	5.3	10.8	–	–	–	–
			Water				
566	603	4	6.3	503	109	4	2.4
728	333	4	8.1	–	–	–	–

For an average partial molecular volume of $NaCl-H_2O$ solution molecules of $\overline{v^{(\alpha)}} \approx 3 \times 10^{-29}\,\mathrm{m}^{-3}$ (see Fig. 6), the equivalent molecular diameter amounts $D^{(\alpha)} = (6\overline{v^{(\alpha)}}/\pi)^{1/3} \approx 3.9\,\text{Å}$, which would correspond to a correlation length in the range $l^{(\star)} \approx (0.9-1.7) \times D^{(\alpha)} = 4-7\,\text{Å}$ adopting the scaling values from Table 1. For $T^{\star}=0.7$ the simulations of Bykov and Zeng (2002) and Napari and Laaksonen (2003) for a planar film reveal a surprisingly good agreement in the values of $K^{(\star)}$ and $l^{(\star)}$. The parameterisation of the characteristic scaling pressure in terms of the spreading coefficient s and $l^{(\star)}$ as $K^{(\star)}=s/l^{(\star)}$ allows a recalculation of the spreading coefficient using the values in Table 2. For a planar interface at $T^{\star}=0.7$ one obtains for argon $s_{\mathrm{BZ}} \approx 0.016\,\mathrm{J\,m^{-2}}$ and $s_{\mathrm{NL}} \approx 0.013\,\mathrm{J\,m^{-2}}$, respectively. These values are very close to each other and are physically plausible. This result suggests the physical reasonability of a dependence $K^{(\star)} = f(s, l^{(\star)})$. However, the observed strong sensitivity of $K^{(\star)}$ against the curvature of the film is a very crucial point in finding an appropriate parameterisation of $K^{(\star)}$ for nanometric particles.

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