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Some mathematical aspects of the Kelvin equation

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Abstract

The complete form of the Kelvin equation, which describes the effect of the interface curvature on the equilibrium vapour pressure in the presence of the relative liquid, is considered. Regularity and general trend of solutions are investigated. A rigorous power-series expansion of the physically meaningful solution is derived by Lagrange's expansion. Our discussion also covers the question of convergence (rate and uniformity) of the appropriate algorithm for numerical estimates. Some mathematical by-products are finally presented.

Keywords: Kelvin equation; Surface tension; Lagrange expansion; Newton–Raphson algorithm; Analytic continuation

1. Introduction

For a one-component liquid–vapour system, the Kelvin equation [1–4] describes the variation of the equilibrium vapour pressure as a function of the curvature of the liquid–vapour interface, eventually in the presence of a gravitational/inertial field. The Kelvin equation is independent of the external field, which only determines the global shape of the liquid–vapour interface, by taking into account the appropriate boundary conditions. For an incompressible liquid of density ρ_ℓ in equilibrium with its own vapour, the most general form of the Kelvin equation at a given point of the liquid–vapour interface can be written as [5]

$$P_v - 2\gamma H - P_0 - \rho_\ell \int_{\rho_v(T,P_0)}^{\rho_v(T,P_v)} \frac{1}{\rho}\frac{\partial P_v}{\partial \rho}(T,\rho)\,\mathrm{d}\rho = 0, \tag{1.1}$$

where:

- T is the temperature of the system;
- H denotes the mean curvature [6] of the interface at the same point;
- P_v stands for the vapour pressure at the same point;

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- $\rho_v = \rho_v(T, P)$ is the equation of state of the vapour phase, describing the vapour density as a function of temperature and pressure;
- γ represents the liquid–vapour surface tension, and here assumed to be essentially dependent on temperature only (as actually it is);
- P_0 denotes the vapour pressure at a point of the interface where the mean curvature H is zero (flat surface).

At a given temperature, Eq. (1.1) relates the equilibrium vapour pressure P_v to the mean curvature H and the equilibrium vapour pressure over a flat interface, P_0. It predicts that the equilibrium vapour pressure changes when the mean curvature of the interface is nonzero. Eq. (1.1) can be derived by purely thermodynamical arguments, but also follows from the conditions of thermomechanical equilibrium of the liquid–vapour system in the presence of an arbitrary stationary gravitational or inertial field [5,7]. If the vapour is approximately described as an ideal gas, the equation of state can be written in terms of the molar mass m of the pure component

$$P_v(T, \rho_v) = \rho_v \frac{RT}{m}$$

where R is the ideal gas constant. The integral in (1.1) is then explicitly calculated

$$\int_{\rho_v(T,P_0)}^{\rho_v(T,P_v)} \frac{1}{\rho} \frac{\partial P_v}{\partial \rho}(T, \rho)\, \mathrm{d}\rho = \int_{P_0 m/RT}^{P_v m/RT} \frac{1}{\rho} \frac{RT}{m}\, \mathrm{d}\rho = \frac{RT}{m} \ln\left(\frac{P_v}{P_0}\right)$$

and the equation takes the form [8]

$$P_v - P_0 - \rho_\ell \frac{RT}{m} \ln\left(\frac{P_v}{P_0}\right) = 2\gamma H.$$

After some manipulation, and remembering that $m/\rho_\ell = v_\ell$, the molar volume of the liquid phase, we obtain

$$P_v - P_0 - \frac{RT}{v_\ell} \ln\left(\frac{P_v}{P_0}\right) = 2\gamma H. \tag{1.2}$$

For a typical component – like water, for instance – the difference $P_v - P_0$ is small in comparison with the logarithmic term, so that it can be neglected in many customary applications. The Kelvin equation reduces then to the classical approximate expression [1,4]

$$\frac{RT}{v_\ell} \ln\left(\frac{P_v}{P_0}\right) = -2\gamma H,$$

whose unique solution leads to the basic Kelvin formula

$$P_v = P_0 \exp\left(-\frac{2\gamma H v_\ell}{RT}\right) \tag{1.3}$$

governing the main dependence of the equilibrium vapour pressure on the mean curvature H of the liquid–vapour interface. Also, whenever the argument of the exponential in (1.3) is very close to zero, the Kelvin equation reduces to the simpler form

$$\frac{P_v - P_0}{P_0} = -\frac{2\gamma H v_\ell}{RT}, \tag{1.4}$$

which is useful for many applications. Along with the Laplace equation, the Kelvin equation constitutes the fundamental relationship of surface chemistry [4], and its validity has been experimentally checked under a wide range of conditions [9–11]. The more rigorous equation (1.2) does not admit a simple solution in terms of elementary functions; approximate solutions have been tentatively proposed in the literature [8], particularly in the physico-chemical description of porous media [7], although essentially on a physical ground and for physical purposes, without any discussion of the more formal, mathematical aspects.

In the present note, we investigate the solutions of the full (1.2), paying particular attention to the problems of existence, regularity, explicit analytical determination and numerical calculation. In doing this, some intriguing mathematical by-products can also be obtained.

2. Analytical and numerical solution of the Kelvin equation

Eq. (1.2) can be rewritten into the equivalent form

$$\frac{v_\ell P_0}{RT}\left(\frac{P_v}{P_0}-1\right)-\ln\left(\frac{P_v}{P_0}\right)=\frac{2\gamma H v_\ell}{RT} \tag{2.1}$$

where $P_v/P_0 \in \mathbb{R}^+$ and both the parameters

$$\alpha=\frac{v_\ell P_0}{RT}\in\mathbb{R}^+ \qquad \beta=\frac{2\gamma H v_\ell}{RT}\in\mathbb{R} \tag{2.2}$$

are typically very small. This seems evident for α, since the molar volume v_v of the vapour phase is much larger than that of the liquid phase at the same pressure and temperature

$$\alpha=\frac{v_\ell P_0}{RT}=\frac{v_v P_0}{RT}\frac{v_\ell}{v_v}=\frac{v_\ell}{v_v}\ll 1,$$

while for the parameter β, we have the identity

$$\beta=\frac{2\gamma H v_\ell}{RT}=\frac{v_\ell P_0}{RT}\frac{2\gamma H}{P_0}=\alpha\frac{2\gamma H}{P_0}$$

with $2\gamma H \ll P_0$. The further substitution $\zeta = P_v/P_0$ allows us to put Eq. (2.1) into the form

$$\alpha(1-\zeta)+\ln\zeta=-\beta \tag{2.3}$$

which, by posing $\zeta = e^{-\alpha-\beta}Q$ and after a short manipulation, reduces to

$$Q=e^{\alpha e^{-\alpha-\beta}Q}.$$

Here, due to their physical meaning, Q and $z=\alpha e^{-\alpha-\beta}$ are both positive numbers. Nevertheless, we can search for the solution in Q of the equation

$$Q=e^{zQ} \tag{2.4}$$

for *arbitrary* $z, Q \in \mathbb{R}$; in doing so, it is clear that the variable Q actually can only be positive. Therefore, we are led to consider the equation

$$Qe^{-zQ}=1 \quad (z,Q)\in\mathbb{R}\times\mathbb{R}^+. \tag{2.5}$$

The properties of the solution Q are illustrated by the proposition below.

Proposition 1. *Let us consider the nonlinear equation*

$$Qe^{-zQ}=1, \quad Q\in\mathbb{R}^+,\ z\in\mathbb{R}. \tag{2.6}$$

Then:

(i) *the set of the solutions Q of (2.6) consists in the graph of two functions*

$$Q_-: z\in(-\infty,1/e] \longrightarrow Q_-(z)\in(0,e]$$
$$Q_+: z\in(0,1/e] \longrightarrow Q_+(z)\in[e,+\infty);$$

(ii) *the function $Q_-(z)$ is increasing and continuous in the whole interval $z\in(-\infty,1/e]$ onto the interval $(0,e]$, and satisfies $Q_-(0)=1$. Moreover, it is analytical in the open interval $z\in(-\infty,1/e)$ onto the open interval $(0,e)$;*

(iii) *$Q_+(z)$ is a decreasing continuous function in the interval $z\in(0,1/e]$ onto the interval $[e,+\infty)$. It is analytical in the open interval $z\in(0,1/e)$ onto $(e,+\infty)$;*

(iv) *the following limits hold*

$$\lim_{z\to 1/e-} \frac{\mathrm{d}Q_-}{\mathrm{d}z}(z) = +\infty \qquad \lim_{z\to 1/e-} \frac{\mathrm{d}Q_+}{\mathrm{d}z}(z) = -\infty.$$

Proof. By inverting Eq. (2.6) with respect to z, we obtain the function

$$z = \frac{\ln Q}{Q} = f(Q)$$

which is analytic $\forall Q \in \mathbb{R}^+$ and whose first derivative can be written as

$$\frac{\mathrm{d}f}{\mathrm{d}Q}(Q) = \frac{1 - \ln Q}{Q^2}.$$

Standard analysis shows then that $f(Q)$ is an analytic increasing function in the interval $Q \in (0, e]$ onto $z \in (-\infty, 1/e)$, while it is decreasing and analytic in the interval $Q \in [e, +\infty)$, with range $z \in (0, 1/e]$. This allows us to introduce the function $Q_-(z)$ as an increasing continuous inverse of $f(Q)$, restricted to $Q \in (0, e]$, onto the interval $z \in (-\infty, 1/e]$. In an analogous way, $Q_+(z)$ will be the decreasing continuous inverse of $f(Q)$ restricted to $Q \in [e, +\infty)$, onto $z \in (0, 1/e]$. The solution set of (2.6) is thus described as the union of the graphs of $Q_-(z)$ and $Q_+(z)$. The analyticity of both $Q_-(z)$ and $Q_+(z)$ in their open domains follows by the Implicit Function Theorem by noting that the analytic function

$$F(z, Q) = -z + f(Q) = -z + \frac{\ln Q}{Q} \quad (z, Q) \in \mathbb{R} \times \mathbb{R}^+$$

has as partial derivative in Q

$$\frac{\partial F}{\partial Q}(z, Q) = \frac{\mathrm{d}f}{\mathrm{d}Q}(Q) = \frac{1 - \ln Q}{Q^2}$$

and satisfies, therefore

$$F(z, Q_-(z)) = 0 \qquad \frac{\partial F}{\partial Q}(z, Q_-(z)) \neq 0 \quad \forall z \in (-\infty, 1/e)$$
$$F(z, Q_+(z)) = 0 \qquad \frac{\partial F}{\partial Q}(z, Q_+(z)) \neq 0 \quad \forall z \in (0, 1/e)$$

since $\mathrm{d}f(Q)/\mathrm{d}Q = 0$ if and only if $Q = e$. Analyticity at $z = 1/e$ can be excluded, in both cases, by proving that functions $Q_-(z)$ and $Q_+(z)$ admit no derivative in $z = 1/e$. If the converse were true, indeed, we would deduce from $F(z, Q_-(z)) = 0$ that

$$-1 + \frac{1 - \ln Q_-(z)}{Q_-(z)^2} \frac{\mathrm{d}Q_-}{\mathrm{d}z}(z) = 0 \quad \forall z \in (-\infty, 1/e]$$

and since $Q_-(1/e) = e$ we would be led to a contradiction. The previous equation is however correct outside the point $z = 1/e$ and provides

$$\frac{\mathrm{d}Q_-}{\mathrm{d}z}(z) = \frac{Q_-(z)^2}{1 - \ln Q_-(z)} \xrightarrow[z\to 1/e-]{} +\infty$$

because $\lim_{z\to 1/e-} Q_-(z) = e$, while $1 - \ln Q_-(z) > 0$ $\forall z \in (-\infty, 1/e)$. The case of $Q_+(z)$ is discussed in an analogous way. □

Out of the previous solutions, only $Q_-(z)$ is physically relevant, being analytic in $z = 0$. For further calculations, we need therefore the power series expansion of the analytic function $Q_-(z)$ in a neighborhood of $z = 0$. This can be achieved by means of Lagrange's expansion [12] by developing an argument due to Case [7].

Proposition 2. *$Q_-(z)$ can be analytically continued in the whole open disc $\{z \in \mathbb{C} : |z| < 1/e\}$, where it satisfies the nonlinear equation $Q_-(z) = e^{zQ_-(z)}$. It can also be continued to the closed disc $\overline{B(0, 1/e)} = \{z \in \mathbb{C} : |z| \leq 1/e\}$ as* *a continuous function, although this is not analytic at $z = 1/e$. The analytic function $Q_-(z)$ has at $z = 0$ the power series expansion*

$$Q_-(z) = \sum_{n=1}^{\infty} \frac{n^n}{n!} z^{n-1} \tag{2.7}$$

convergent $\forall z \in \overline{B(0, 1/e)}$.

Proof. At fixed $w \in \mathbb{R}$, let us consider the equation in H

$$H = \varepsilon\, e^{wH}. \tag{2.8}$$

For ε sufficiently close to zero, any equation of the form

$$H = \lambda + \varepsilon\, \Phi(H)$$

with analytic $\Phi(H)$, defines H as an analytic function of ε, which can be expressed by Lagrange's expansion [12]

$$H = \lambda + \sum_{n=1}^{\infty} \frac{\varepsilon^n}{n!} \left(\frac{\mathrm{d}}{\mathrm{d}H}\right)^{n-1} [\Phi(H)^n] \Big|_{H=\lambda}.$$

Its application to Eq. (2.8) provides then the identity

$$H = \sum_{n=1}^{\infty} \frac{\varepsilon^n}{n!} \left(\frac{\mathrm{d}}{\mathrm{d}H}\right)^{n-1} (e^{nwH}) \Big|_{H=0} = \sum_{n=1}^{\infty} \frac{\varepsilon^n}{n!} n^{n-1} w^{n-1}$$

which must be valid for $|\varepsilon|$ small enough. On the other hand, by posing $H = \varepsilon Q$, we get the power series expansion

$$Q = \frac{1}{\varepsilon} \sum_{n=1}^{\infty} \frac{\varepsilon^n}{n!} n^{n-1} w^{n-1} = \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!} (\varepsilon w)^{n-1} \tag{2.9}$$

which must describe, in an appropriate neighbourhood of $\varepsilon = 0$, an analytic function of ε solution of the equation

$$\varepsilon Q = \varepsilon\, e^{w\varepsilon Q} \iff Q = e^{w\varepsilon Q} \tag{2.10}$$

equivalent to (2.8). Actually, both Eq. (2.10) and the series solution (2.9) depend on the variable $z = w\varepsilon$, so it is z that must be small enough. We conclude that

$$Q = \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!} z^{n-1}$$

describes the power series solution, analytic in a neighbourhood of $z = 0$, of the equation

$$Q = e^{zQ}.$$

From Proposition 1, it is known that such a solution, analytical in a real neighbourhood of $z = 0$, is given by $Q_-(z)$, so that

$$Q_-(z) = \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!} z^{n-1} = \sum_{k=0}^{\infty} \frac{(k+1)^k}{(k+1)!} z^k \tag{2.11}$$

for any z sufficiently close to zero. Since $Q_-(z)$ is not analytic at $z = 1/e$, we expect that the series on the right-hand side of (2.11) has a radius of convergence not larger than $1/e$. Denoted by a_k the k-th coefficient of the series, via Stirling's asymptotic formula, for large k's we obtain

$$|a_k|^{1/k} = \left[\frac{(k+1)^k}{(k+1)!}\right]^{1/k} \sim \left[\frac{(k+1)^k\, e^{k+1}}{\sqrt{2\pi(k+1)}(k+1)^{k+1}}\right]^{1/k} = \left[\frac{1}{\sqrt{2\pi}(k+1)^{3/2}} e^{k+1}\right]^{1/k}$$

so that there exists the limit

$$\lim_{k\to+\infty} |a_k|^{1/k} = \lim_{k\to+\infty} \left(\frac{1}{2\pi}\right)^{1/2k} \frac{1}{(k+1)^{3/2k}}\, e^{1+\frac{1}{k}} = e$$

and the radius of convergence follows from Hadamard's formula

$$\rho = \frac{1}{\limsup\limits_{k\to+\infty} |a_k|^{1/k}} = \frac{1}{\lim\limits_{k\to+\infty} |a_k|^{1/k}} = \frac{1}{e}.$$

As a consequence, the right-hand side of Eq. (2.11) defines an analytic function of z within the disk of convergence

$$B(0, 1/e) = \{z \in \mathbb{C} : |z| < 1/e\}$$

and, in particular, in the open interval $(0, 1/e)$. The Identity Principle of analytic functions implies then that the identity (2.11) actually extends to the whole disk $B(0, 1/e)$ and that the analytic equation

$$Q_-(z) = e^{zQ_-(z)}$$

holds true in the same disk as a complex equation.

We have already proved in Proposition 1 that $Q_-(z)$ is continuous at $z = 1/e$ and that $Q_-(1/e) = e$. Thus, in order to prove that (2.11) also holds at $z = 1/e$, we simply have to show that the power series in (2.11) converges at $z = 1/e$, since if this is the case the power series converges uniformly in $z \in [0, 1/e]$ by Abel's theorem and the limit function must be continuous in the whole interval $[0, 1/e]$. To prove the convergence of the series

$$\sum_{n=1}^{\infty} \frac{n^{n-1}}{n!} \frac{1}{e^{n-1}} = \sum_{k=0}^{\infty} \frac{(k+1)^k}{(k+1)!} \frac{1}{e^k} \tag{2.12}$$

we denote with b_k its k-th term, and reckon the expression

$$k\left(\frac{b_k}{b_{k+1}} - 1\right) = k\left[e\left(\frac{k}{k+1}\right)^{k-1} - 1\right] = \left(1 + \frac{1}{k}\right)^{-(k-1)} k\left[e - \left(1 + \frac{1}{k}\right)^{k-1}\right]$$

where

$$\begin{aligned} k\left[e - \left(1 + \frac{1}{k}\right)^{k-1}\right] &= k\left[e - e^{(k-1)\ln(1+\frac{1}{k})}\right] = ek\left[1 - e^{-1+(k-1)\ln(1+\frac{1}{k})}\right] \\ &= ek\left[1 - e^{-1+(k-1)\left[\frac{1}{k} - \frac{1}{2k^2} + O(\frac{1}{k^3})\right]}\right] = ek\left[1 - e^{-\frac{3}{2k} + O(\frac{1}{k^2})}\right] \\ &= ek\left[1 - 1 + \frac{3}{2k} + O\left(\frac{1}{k^2}\right)\right] = \frac{2}{3}e + O\left(\frac{1}{k}\right) \quad (k \to +\infty) \end{aligned}$$

so that

$$\lim_{k\to+\infty} k\left(\frac{b_k}{b_{k+1}} - 1\right) = e^{-1}\frac{3}{2}e = \frac{3}{2}$$

and since the final limit is greater than 1, the positive-term series (2.12) converges by Raabe's test. Absolute convergence on the disk boundary $\{z \in \mathbb{C} : |z| = 1/e\}$ now follows from the convergence of the series at $z = 1/e$, since the series has only positive coefficients; by Abel's theorem convergence is uniform within any closed sector $\mathbb{S} \subset \overline{B(0, 1/e)}$ having its vertex at a point of the disk boundary, so that the limit function is continuous. In particular, the limit of (2.12) is precisely $Q(1/e) = e$

$$\sum_{n=1}^{\infty} \frac{n^{n-1}}{n!} \frac{1}{e^{n-1}} = e.$$

By Proposition 1, however, the function $Q_-(z)$ is not analytic at $z = 1/e$. □

The previous series expansion is particularly useful for theoretical considerations. For numerical purposes, however, (2.7) provides an efficient way to calculate $Q_-(z)$ only when z is sufficiently close to zero. Whenever $|z| \simeq 1/e$, or $z \in (-\infty, -1/e)$, the following Proposition 3 suggests a more convenient strategy.

Proposition 3. *In the interval $z \in (-\infty, 1/e)$, the function $Q_-(z)$ can be defined as the limit of a sequence of functions $Q_n(z)$ in the same interval*

$$Q_-(z) = \lim_{n\to+\infty} Q_n(z)$$

where $Q_0(z) = 1/(1-z)$ and

$$Q_{n+1}(z) = Q_n(z)\frac{1 - 2\ln Q_n(z) + zQ_n(z)}{1 - \ln Q_n(z)} \quad \forall n \in \mathbb{N}.$$

At any fixed $z \in (-\infty, 1/e)$, $[Q_n(z)]_{n\in\mathbb{N}}$ constitutes a growing sequence and the convergence is of order 2. For fixed $n \in \mathbb{N}$, $Q_n(z)$ is an increasing function of $z \in (-\infty, 1/e)$. Convergence is uniform in any compact interval $[a, b] \subset (-\infty, 1/e)$.

Proof. The first and the second derivatives of the function $f(Q) = \ln Q/Q$ are expressed as

$$\frac{\mathrm{d}f(Q)}{\mathrm{d}Q} = \frac{1 - \ln Q}{Q^2} \qquad \frac{d^2 f(Q)}{\mathrm{d}Q^2} = \frac{2}{Q^3}\left(-\frac{3}{2} + \ln Q\right)$$

and from the negative sign of the second derivative we conclude that $f(Q)$ is a concave function of $Q \in (0, e)$ onto $(-\infty, 1/e)$; in the same interval the first derivative is strictly positive. For any $z \in (-\infty, 1/e)$, $Q_-(z)$ is the solution in $(0, e)$ of the equation $f(Q) = z$ or, equivalently, of

$$Q_-(z) = e^{zQ_-(z)} \quad \forall z \in (-\infty, 1/e)$$

which implies the inequality

$$Q_-(z) = e^{zQ_-(z)} > 1 + zQ_-(z)$$

and finally

$$\frac{1}{1-z} < Q_-(z) \quad \forall z \in (-\infty, 1/e). \tag{2.13}$$

As a consequence, the solution in $Q = Q_-(z) \in (0, e)$ of $f(Q) - z = 0$ for any fixed $z \in (-\infty, 1/e)$ can be determined by the Newton–Raphson method

$$Q_{n+1} = Q_n - \frac{f(Q_n) - z}{f'(Q_n)} = Q_n\frac{1 - 2\ln Q_n + zQ_n}{1 - \ln Q_n}$$

starting the algorithm at any point $Q_0 < Q_-(z)$; if this is the case, the sequence Q_n is increasing. Moreover, since $f'(Q_-(z)) > 0$, the algorithm converges quadratically — order 2 convergence. By inequality (2.13), we simply have to pose $Q_0(z) = 1/(1-z)$, thus defining the increasing sequence $[Q_n(z)]_{n\in\mathbb{N}}$. As a by-product, we also obtain that $Q_n(z) < Q_-(z)$ and $f(Q_n(z)) < z$ $\forall n \in \mathbb{N}$ and $\forall z \in (-\infty, 1/e)$. The monotonicity of $Q_n(z)$ at fixed n easily follows by induction by deriving the recursion relationship

$$Q_{n+1}(z) = Q_n(z) + \frac{z - f(Q_n(z))}{f'(Q_n(z))} \tag{2.14}$$

with respect to z

$$\begin{aligned}\frac{\mathrm{d}Q_{n+1}}{\mathrm{d}z}(z) &= \frac{\mathrm{d}Q_n}{\mathrm{d}z}(z) - [z - f(Q_n(z))]\frac{f''(Q_n(z))}{[f'(Q_n(z))]^2}\frac{\mathrm{d}Q_n}{\mathrm{d}z}(z) + \frac{1 - f'(Q_n(z))\frac{\mathrm{d}Q_n}{\mathrm{d}z}(z)}{f'(Q_n(z))}\\ &= \frac{1}{f'(Q_n(z))} + [z - f(Q_n(z))]\frac{[-f''(Q_n(z))]}{[f'(Q_n(z))]^2}\frac{\mathrm{d}Q_n}{\mathrm{d}z}(z)\end{aligned} \tag{2.15}$$

and noting that

$$f'(Q_n(z)) > 0, \qquad z - f(Q_n(z)) > 0, \qquad -f''(Q_n(z)) > 0 \quad \forall z \in (-\infty, 1/e),\ n \in \mathbb{N}$$

the latter inequality being due to $f''(Q) < 0\ \forall Q \in (0, e)$, as previously discussed. If $\mathrm{d}Q_n(z)/\mathrm{d}z$ is assumed to be positive in $z \in (-\infty, 1/e)$ for a given n, then (2.15) implies that the same holds true also for $\mathrm{d}Q_{n+1}(z)/\mathrm{d}z$. The requirement is actually verified for $n = 0$, since

$$\frac{\mathrm{d}Q_0}{\mathrm{d}z}(z) = \frac{\mathrm{d}}{\mathrm{d}z}\left(\frac{1}{1-z}\right) = \frac{1}{(1-z)^2} > 0 \quad \forall z \in (-\infty, 1/e)$$

so induction works and $Q_n(z)$ is a growing function of $z \in (-\infty, 1/e)$ at any fixed $n \in \mathbb{N}$. The uniformity of the convergence in any compact interval $[a, b] \subset (-\infty, 1/e)$ of z stems from an appropriate manipulation of the recurrence (2.14) which, owing to identity $f(Q_-(z)) = z$, can be written as

$$Q_{n+1}(z) - Q_-(z) = Q_n(z) - Q_-(z) + \frac{f(Q_-(z)) - f(Q_n(z))}{f'(Q_n(z))}$$

or, by Mean Value Theorem,

$$\begin{aligned} Q_{n+1}(z) - Q_-(z) &= Q_n(z) - Q_-(z) + \frac{f'(Q^\star(z))}{f'(Q_n(z))}[Q_-(z) - Q_n(z)] \\ &= [Q_n(z) - Q_-(z)]\left[1 - \frac{f'(Q^\star(z))}{f'(Q_n(z))}\right] \end{aligned}$$

for a suitable choice of $Q^\star(z) \in (Q_n(z), Q_-(z))$. In the final expression

$$Q_-(z) - Q_{n+1}(z) = [Q_-(z) - Q_n(z)]\left[1 - \frac{f'(Q^\star(z))}{f'(Q_n(z))}\right]$$

both the differences $Q_-(z) - Q_{n+1}(z)$ and $Q_-(z) - Q_n(z)$ are strictly positive, while the residual factor is positive and admits the bound

$$1 - \frac{f'(Q^\star(z))}{f'(Q_n(z))} \le 1 - \frac{f'(Q_-(z))}{f'(Q_n(z))} \le 1 - \frac{f'(Q_-(z))}{f'(Q_0(z))} \quad \forall z \in (-\infty, 1/e),\ n \in \mathbb{N}$$

due to $Q^\star(z) < Q_-(z)$ and to the decreasing monotonicity of $f'(Q) > 0$ in $Q \in (0, e)$. For any compact interval $[a, b] \subset (-\infty, 1/e)$, we have therefore

$$\begin{aligned} \sup_{z\in[a,b]} |Q_-(z) - Q_{n+1}(z)| &= \sup_{z\in[a,b]} [Q_-(z) - Q_{n+1}(z)] \\ &\le \sup_{z\in[a,b]} [Q_-(z) - Q_n(z)] \sup_{z\in[a,b]}\left[1 - \frac{f'(Q_-(z))}{f'(Q_0(z))}\right] \\ &= \sup_{z\in[a,b]} |Q_-(z) - Q_n(z)| \sup_{z\in[a,b]}\left[1 - \frac{f'(Q_-(z))}{f'(Q_0(z))}\right] \end{aligned} \tag{2.16}$$

where the extremum involving derivatives can be expressed in a more convenient form by the change of variable $z = f(Q) = \ln Q/Q$, inverse of $Q = Q_-(z)$,

$$\begin{aligned} \sup_{z\in[a,b]}\left[1 - \frac{f'(Q_-(z))}{f'(Q_0(z))}\right] &= \sup_{z\in[a,b]}\left\{1 - \frac{1 - \ln Q_-(z)}{Q_-(z)^2}\left[\frac{1 + \ln(1-z)}{(1-z)^{-2}}\right]^{-1}\right\} \\ &= \sup_{Q\in[Q_-(a),Q_-(b)]}\left\{1 - \frac{1-\ln Q}{Q^2}\left[\frac{1+\ln(1-z)}{(1-z)^{-2}}\right]^{-1}\Bigg|_{z=\ln Q/Q}\right\} \end{aligned}$$

with $[Q_-(a), Q_-(b)] \subset (0, e)$. The graph of the function

$$M(Q) = 1 - \frac{1-\ln Q}{Q^2}\left[\frac{1+\ln(1-z)}{(1-z)^{-2}}\right]^{-1}\Bigg|_{z=\ln Q/Q} \tag{2.17}$$

on the open interval $Q \in (0, e)$ can be easily investigated by lengthy, standard and not particularly deep arguments, and its general trend is illustrated in Fig. 1. In particular, the function is continuous and strictly positive in

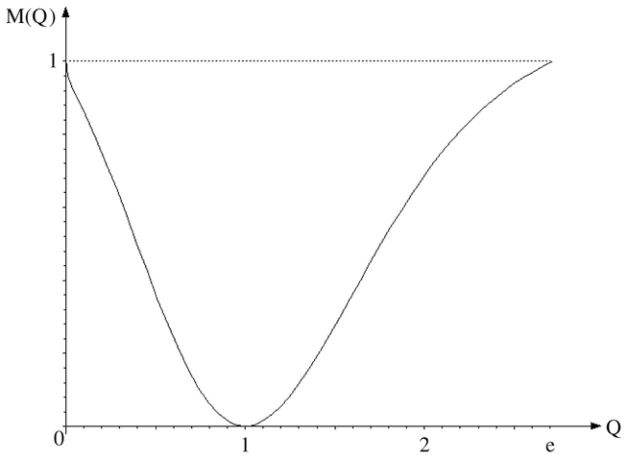

Fig. 1. Graph of the auxiliary function $M(Q)$ involved in the proof of Proposition 3 — see Eq. (2.17).

the whole interval $(0, e)$ except at point $Q = 1$. Moreover it has range $(0, 1)$, with $\lim_{Q\to 0+} M(Q) = 1$ and $\lim_{Q\to e-} M(Q) = 1$. These conditions imply that for any $[Q_-(a), Q_-(b)] \subset (0, e)$, there holds

$$\sup_{Q\in[Q_-(a),Q_-(b)]} M(Q) = C_{ab} < 1$$

so that inequality (2.16) becomes

$$\sup_{z\in[a,b]} |Q_-(z) - Q_{n+1}(z)| \le \sup_{z\in[a,b]} |Q_-(z) - Q_n(z)|\, C_{ab} \quad n \in \mathbb{N},$$

and by iterating the same formula, we get

$$\sup_{z\in[a,b]} |Q_-(z) - Q_{n+1}(z)| \le \sup_{z\in[a,b]} |Q_-(z) - Q_0(z)|\, C_{ab}^{n+1} \quad \forall n \in \mathbb{N}.$$

Whence we conclude that the convergence is uniform on any $[a, b] \subset (-\infty, 1/e)$, and with an exponential rate. □

By applying Proposition 2, the Kelvin equation can be solved with respect to the pressure ratio P_v/P_0 by means of an appropriate power series expansion.

Proposition 4. *By posing*

$$\alpha = \frac{v_\ell P_0}{RT} \in \mathbb{R}^+ \qquad \beta = \frac{2\gamma H v_\ell}{RT} \in \mathbb{R},$$

$\forall\alpha > 0$ *and* $\forall\beta \ge 1 - \alpha + \ln\alpha$ *the Kelvin equation* (2.1) *can be explicitly solved with respect to the pressure ratio* P_v/P_0 *and we can write*

$$\frac{P_v}{P_0} = \zeta = e^{-\alpha-\beta} Q_-(\alpha e^{-\alpha-\beta}) = e^{-\alpha-\beta} \sum_{k=1}^{\infty} \frac{k^{k-1}}{k!} (\alpha e^{-\alpha-\beta})^{k-1}. \tag{2.18}$$

Proof. We simply have to recall that if we pose $P_v/P_0 = \zeta = e^{-\alpha-\beta} Q$ and $z = \alpha e^{-\alpha-\beta}$, then the unknown function Q must obey $Q = e^{zQ}$. For α and β close to zero, the pressure ratio must be around 1; as a consequence $Q = Q_-(z) = Q_-(\alpha e^{-\alpha-\beta})$ and, finally, $P_v/P_0 = e^{-\alpha-\beta} Q_-(\alpha e^{-\alpha-\beta})$. By replacing expansion (2.7), we derive (2.18). The parameter α is assumed to be positive for physical reasons, but the convergence of the series in (2.18) imposes the further requirement

$$\alpha e^{-\alpha-\beta} \le 1/e$$

and therefore $\beta \ge 1 - \alpha + \ln\alpha$. By the way, it is noticeable that $1 - \alpha + \ln\alpha \le 0\ \forall\alpha > 0$ and that $1 - \alpha + \ln\alpha \ll 0$ in a right neighborhood of $\alpha = 0$ — we have already stressed that, typically, $\alpha \gtrsim 0$. □

3. Particular cases and mathematical implications

The case of a flat liquid–vapour interface – $H = 0$ – falls in the domain of application of formula (2.18), since $H = 0$ implies $\beta = 0$, while

$$\alpha e^{-\alpha} \le 1/e \quad \forall \alpha > 0$$

as it can be easily verified by studying the graph of the function $\alpha e^{-\alpha}$ in $\alpha \in \mathbb{R}^+$. In these circumstances, the following proposition is useful.

Proposition 5. *The function*

$$\Xi(\alpha) = e^{-\alpha} Q_-(\alpha\, e^{-\alpha}) = e^{-\alpha} \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!} (\alpha e^{-\alpha})^{n-1} \tag{3.1}$$

(i) *is defined* $\forall \alpha > 0$;
(ii) *is analytic* $\forall \alpha \in \mathbb{R}^+ \setminus \{+1\}$;
(iii) *satisfies the condition* $\Xi(\alpha) = 1\ \forall \alpha \in (0, 1)$;
(iv) *is a monotonic decreasing function in the interval* $\alpha > 1$;
(v) *tends to zero in the limit* $\alpha \to +\infty$;
(vi) *is not analytic at* $\alpha = 1$;
(vii) *defines an analytic function of the open domain*

$$\{\alpha \in \mathbb{C} : |\alpha|\, e^{1-\Re e(\alpha)} < 1\}$$

whose restriction to the open connected set

$$\{\alpha \in \mathbb{C} : |\alpha|\, e^{1-\Re e(\alpha)} < 1, \Re e(\alpha) < 1\}$$

is constant at the value 1.

Proof. Item (i) easily follows by noting that $\alpha e^{-\alpha} \le e^{-1}\ \forall \alpha > 0$ and using Proposition 2 for the function $Q_-(z)$. Property (ii) is obvious, since $\mathbb{R}_+ \setminus \{+1\} = \{\alpha > 0 : \alpha e^{-\alpha} < e^{-1}\}$, open interval where $Q_-(z)$ is analytic by Proposition 2. The bizarre property (iii) holds because $\forall \alpha > 0$ $Q_-(\alpha e^{-\alpha}) = e^{\alpha} \Xi(\alpha)$ is, by definition, the only solution in Q of the equation

$$Q = e^{\alpha e^{-\alpha} Q}, \quad Q \in (0, e),$$

so that $\Xi(\alpha) = e^{-\alpha} Q_-(\alpha e^{-\alpha})$ provides the unique solution in X of

$$e^{-\alpha X} X = e^{-\alpha}, \qquad X \in (0, e^{1-\alpha}). \tag{3.2}$$

As a simple analysis shows, for any fixed $\alpha > 0$ the function $L_\alpha(X) = e^{-\alpha X} X$ is positive on the interval $X > 0$, increasing in $X \in (0, 1/\alpha)$ and decreasing in $X \in (1/\alpha, +\infty)$; moreover, it has a unique absolute maximum at $X = 1/\alpha$, with value $1/\alpha e$, and admits the limits $\lim_{X\to 0+} L_\alpha(X) = 0$, $\lim_{X\to+\infty} L_\alpha(X) = 0$. These properties, along with the bound $\alpha e^{-\alpha} \le e^{-1}\ \forall \alpha > 0$, imply that the Eq. (3.2) has precisely two solutions $\forall \alpha \in \mathbb{R}^+ \setminus \{+1\}$, one in $(0, 1/\alpha)$ and one in $(1/\alpha, +\infty)$. The first solution is thus $\Xi(\alpha) \in (0, e^{1-\alpha}) \subset (0, 1/\alpha)$. Whenever $\alpha \in (0, 1)$, the inequality $e^{1-\alpha} > 1$ holds, and the solution reduces to $X = 1$, since $L_\alpha(1) = e^{-\alpha}$ anyway. Therefore $\Xi(\alpha) = 1\ \forall \alpha \in (0, 1)$. Notice that the argument fails for $\alpha > 1$, because in this case $e^{1-\alpha} < 1$ and consequently $1 \notin (0, e^{1-\alpha})$ — actually $X = 1$ is the unique solution in $(1/\alpha, +\infty)$.

The function is monotonic decreasing $\forall \alpha > 1$ – item (iv) – because $e^{-\alpha}$ is decreasing, the series $Q_-(\alpha e^{-\alpha})$ has only positive terms, and $\alpha e^{-\alpha}$ is decreasing $\forall \alpha > 1$. Convergence to zero in the limit $\alpha \to +\infty$ – item (v) – stems from the analyticity, and thus the continuity, of $Q_-(z)$ at $z = 0$:

$$\lim_{\alpha\to+\infty} \Xi(\alpha) = \lim_{\alpha\to+\infty} e^{-\alpha} Q_-(\alpha e^{-\alpha}) = \lim_{\alpha\to+\infty} e^{-\alpha} \lim_{\alpha\to+\infty} Q_-(\alpha e^{-\alpha}) = 0\, Q_-(0) = 0.$$

Statement (vi) follows from the Identity Principle of holomorphic functions: if Ξ were analytic also in $\alpha = 1$, then it would be analytic on the whole half-line $\alpha > 0$, and since $\Xi(\alpha) - 1 = 0\ \forall \alpha \in (0, 1)$, any point of the interval

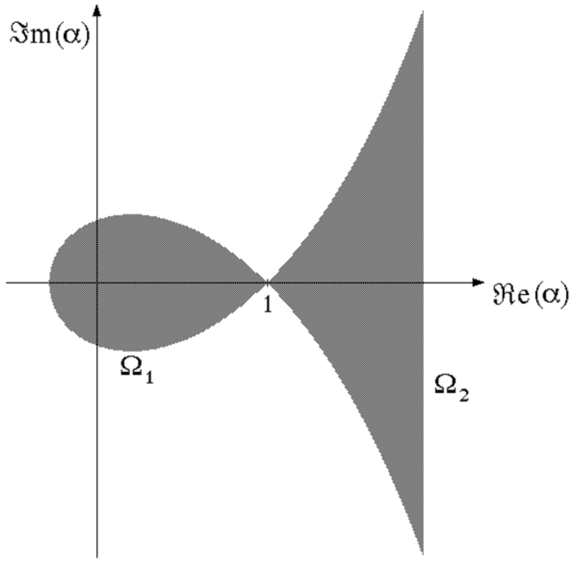

Fig. 2. The domains Ω_1 and Ω_2 of the complex plane considered in the proof of Proposition 5, item (vii). Restricted to the open region Ω_1, the function $\Xi(\alpha)$ defined by the analytical continuation of (3.1) is constant at the value 1.

$\alpha \in (0, 1)$ would constitute a limit point of a sequence of zeros of the analytic function $\Xi(\alpha) - 1 = 0$. As a consequence, we would have

$$\Xi(\alpha) - 1 = 0 \quad \forall \alpha > 0,$$

contradicting the monotonicity of $\Xi(\alpha)$ for $\alpha > 1$. Finally, property (vii) arises owing to analyticity of Q in the disc $\{z \in \mathbb{C} : |z| < e^{-1}\}$, so that $\Xi(\alpha)$ is certainly holomorphic $\forall \alpha \in \mathbb{C}$ obeying $|\alpha e^{-\alpha}| < e^{-1}$ or, equivalently, $|\alpha| e^{1-\Re e(\alpha)} < 1$. The latter domain consists in the disjoint union of two connected open sets

$$\Omega_1 = \{\alpha \in \mathbb{C} : |\alpha| e^{1-\Re e(\alpha)} < 1, \Re e(\alpha) < 1\}$$

and

$$\Omega_2 = \{\alpha \in \mathbb{C} : |\alpha| e^{1-\Re e(\alpha)} < 1, \Re e(\alpha) > 1\}$$

the first containing the whole segment (0, 1) of the real axis, where $\Xi(\alpha) = 1$. The Identity Principle implies then that $\Xi(\alpha) = 1 \; \forall \alpha \in \Omega_1$. The general portrait of the sets Ω_1 and Ω_2 is illustrated in Fig. 2. Notice that it is impossible to define an analytical continuation of Ξ from the domain Ω_1 to the region Ω_2 through the residual complex plane for if it were, Ξ would be constant also along the half-line $\alpha > 0$, a contradiction. □

As a consequence of the previous Proposition 5, the graph of the function $\Xi(\alpha)$ for $\alpha > 0$ has the general trend sketched in Fig. 3.

Since in the Kelvin equation (2.1) the parameter α is positive and (typically much) smaller than 1, we conclude that

Proposition 6. *For a flat liquid–vapour interface – $H = 0$ – the only solution of the Kelvin equation*

$$\frac{v_\ell P_0}{RT}\left(\frac{P_v}{P_0} - 1\right) - \ln\left(\frac{P_v}{P_0}\right) = \frac{2\gamma H v_\ell}{RT}$$

with respect to the pressure ratio P_v/P_0 in the interval $[0, 1/\alpha)$, $\alpha = v_\ell P_0/RT < 1$, is the trivial one

$$P_v/P_0 = 1.$$

The latter result expresses, obviously, the physical statement that over a flat liquid–vapour interface at equilibrium, the surface tension does not affect the vapour pressure.

From (2.18), remembering that $P_v/P_0 = 1$ at $\beta = 0$, it is straightforward to deduce further that

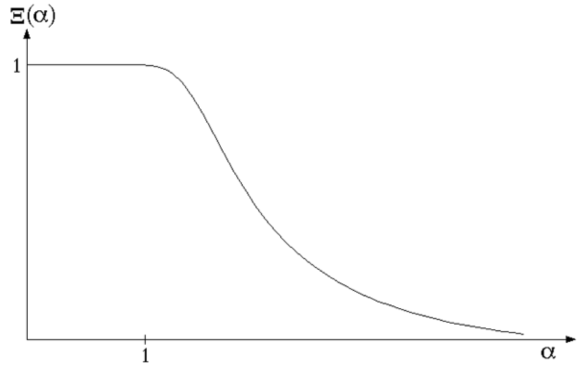

Fig. 3. The graph of the function $\Xi(\alpha)$ in the positive real half-axis. Notice the constancy in the interval $\alpha \in (0, 1)$ and the lack of analyticity at $\alpha = 1$.

Proposition 7. *For any fixed $\alpha > 0$, the pressure ratio P_v/P_0 is a decreasing monotonic function of $\beta \in [1 - \alpha + \ln\alpha, +\infty)$. In particular, $P_v/P_0 < 1$ for $\beta > 0$ and $P_v/P_0 > 1$ when $\beta < 0$.*

This statement means that when the interface curvature H is negative, the vapour pressure at equilibrium P_v must be less than that valid for a flat interface; this is the case, for instance, of a liquid which wets the walls of a capillary where it is contained — the equilibrium contact angle is smaller than 90 deg. In contrast, when H is positive, the equilibrium vapour pressure increases with respect to the value over a flat interface — like for a liquid in a capillary with an equilibrium contact angle greater than 90 deg.

The dependence on β is conveniently described by the following.

Proposition 8. *For fixed $\alpha > 0$, the function defined by the series*

$$\zeta(\beta) = e^{-\alpha-\beta}\, Q_-(\alpha e^{-\alpha-\beta}) = e^{-\alpha-\beta} \sum_{k=1}^{\infty} \frac{k^{k-1}}{k!} (\alpha\, e^{-\alpha-\beta})^{k-1}$$

satisfies the properties listed below:

(i) $\forall\alpha > 0$ $\zeta(\beta)$ *is analytic in the complex half-plane*

$$\{\beta \in \mathbb{C} : \Re e(\beta) > 1 - \alpha + \ln\alpha\};$$

(ii) $\forall\alpha \in (0, 1)$ *and* $\forall\alpha > 1$, *the function can be expanded into a power series in a neighbourhood of* $\beta = 0$, *with radius of convergence*

$$|1 - \alpha + \ln\alpha| = -1 + \alpha - \ln\alpha;$$

(iii) $\forall\beta \in \mathbb{C}$, $|\beta| < -1 + \alpha - \ln\alpha$, *the function* $\zeta(\beta)$ *can be written in the form*

$$\zeta(\beta) = e^{-\beta} \sum_{n=0}^{\infty} (-1)^n \frac{\beta^n}{n!} e^{-\alpha} \sum_{k=1}^{\infty} \frac{k^{k-1}}{k!} (\alpha e^{-\alpha})^{k-1} (k-1)^n. \tag{3.3}$$

Proof. Indeed, due to Proposition 2, the series $Q(\alpha e^{-\alpha-\beta})$ is certainly convergent within the convergence radius at zero

$$|\alpha e^{-\alpha-\beta}| = \alpha e^{-\alpha-\Re e(\beta)} < e^{-1}$$

that is, $\forall\beta \in \mathbb{C}$ such that $\ln\alpha - \alpha - \Re e(\beta) < -1$. The same Proposition 2 excludes that analyticity occurs at $\beta = 1 - \alpha + \ln\alpha < 0$; thus by Cauchy's integral formula, $\zeta(\beta)$ can be expanded into a power series in $\beta = 0$ with radius of convergence $|1 - \alpha + \ln\alpha|$; the latter vanishes when $\alpha = 1$, a case which must be excluded. The same properties extend to the auxiliary function $X(\beta) = e^{\beta}\zeta(\beta) = e^{-\alpha} Q_-(\alpha e^{-\alpha-\beta})$. The derivatives of $X(\beta)$ can then be calculated by the series

$$\frac{\mathrm{d}^n X}{\mathrm{d}\beta^n}(\beta) = (-1)^n e^{-\alpha} \sum_{k=1}^{\infty} \frac{k^{k-1}}{k!} (\alpha e^{-\alpha})^{k-1} (k-1)^n e^{-\beta(k-1)}$$

which at $\beta = 0$ reduce to

$$\frac{\mathrm{d}^n X}{\mathrm{d}\beta^n}(0) = (-1)^n e^{-\alpha} \sum_{k=1}^{\infty} \frac{k^{k-1}}{k!} (\alpha e^{-\alpha})^{k-1} (k-1)^n \tag{3.4}$$

and allow us to write, $\forall \beta \in \mathbb{C}$, $|\beta| < -1 + \alpha - \ln \alpha$,

$$X(\beta) = \sum_{n=0}^{\infty} \frac{\beta^n}{n!} \frac{\mathrm{d}^n X}{\mathrm{d}\beta^n}(0) = \sum_{n=0}^{\infty} (-1)^n \frac{\beta^n}{n!} e^{-\alpha} \sum_{k=1}^{\infty} \frac{k^{k-1}}{k!} (\alpha e^{-\alpha})^{k-1} (k-1)^n, \tag{3.5}$$

so completing the proof. □

There is an intriguing way to calculate the derivatives of the auxiliary function $X(\beta)$ at $\beta = 0$ and, consequently, the inner series in the right-hand side of (3.5).

Proposition 9. *For any $\alpha \in (0, 1)$, the following relations are satisfied:*

$$\text{(i)}\ \frac{\mathrm{d}^{n+1} X}{\mathrm{d}\beta^{n+1}}(0) = -\frac{1}{1-\alpha} \left\{ \sum_{j=0}^{n-1} \binom{n}{j} \frac{\mathrm{d}^{j+1} X}{\mathrm{d}\beta^{j+1}}(0) \left[1 - \alpha \frac{\mathrm{d}^{n-j} X}{\mathrm{d}\beta^{n-j}}(0) \right] + \alpha \sum_{j=0}^{n} \binom{n}{j} \frac{\mathrm{d}^{j} X}{\mathrm{d}\beta^{j}}(0) \frac{\mathrm{d}^{n-j} X}{\mathrm{d}\beta^{n-j}}(0) \right\} \quad \forall n = 1, 2, \ldots \tag{3.6a}$$

$$\text{(ii)}\ \sum_{k=1}^{\infty} \frac{k^{k-1}}{k!} (\alpha e^{-\alpha})^{k-1} (k-1)^n = (-1)^n e^{\alpha} c_n(\alpha) \quad \forall n = 0, 1, 2, \ldots \tag{3.6b}$$

where $c_0(\alpha) = 1$, $c_1(\alpha) = -\alpha/(1-\alpha)$ and the recurrence

$$c_{n+1}(\alpha) = -\frac{1}{1-\alpha} \left\{ \sum_{j=0}^{n-1} \binom{n}{j} c_{j+1}(\alpha) \left[1 - \alpha c_{n-j}(\alpha) \right] + \alpha \sum_{j=0}^{n} \binom{n}{j} c_j(\alpha) c_{n-j}(\alpha) \right\} \quad \forall n = 1, 2, \ldots \tag{3.6c}$$

defines the subsequent coefficients.

Proof. By inserting $\zeta = e^{-\beta} X(\beta)$ in Eq. (2.3), we obtain

$$\ln X(\beta) = -\alpha + \alpha e^{-\beta} X = \alpha[e^{-\beta} X(\beta) - 1] \tag{3.7}$$

where $X(\beta)$ is an analytic nonvanishing function of β in a neighbourhood of $\beta = 0$ and, if $\alpha \in (0, 1)$, $X(0) = \Xi(\alpha) = 1$ by Proposition 5. The derivation side by side of (3.7) leads to the relationship

$$\frac{\mathrm{d}X}{\mathrm{d}\beta}(\beta)[e^{\beta} - \alpha X(\beta)] = -\alpha X(\beta)^2. \tag{3.8}$$

The general recurrence relation (3.6a) follows by deriving n times term-by-term Eq. (3.8), and applying the Leibnitz rule for iterated derivatives

$$\sum_{j=0}^{n} \binom{n}{j} \left(\frac{\mathrm{d}}{\mathrm{d}\beta} \right)^j \left(\frac{\mathrm{d}X}{\mathrm{d}\beta} \right) \cdot \left(\frac{\mathrm{d}}{\mathrm{d}\beta} \right)^{n-j} (e^{\beta} - \alpha X) = -\alpha \sum_{j=0}^{n} \binom{n}{j} \frac{\mathrm{d}^j X}{\mathrm{d}\beta^j} \frac{\mathrm{d}^{n-j} X}{\mathrm{d}\beta^{n-j}}$$

which provides the formula

$$\sum_{j=0}^{n} \binom{n}{j} \frac{\mathrm{d}^{j+1} X}{\mathrm{d}\beta^{j+1}} \left(e^{\beta} - \alpha \frac{\mathrm{d}^{n-j} X}{\mathrm{d}\beta^{n-j}} \right) = -\alpha \sum_{j=0}^{n} \binom{n}{j} \frac{\mathrm{d}^j X}{\mathrm{d}\beta^j} \frac{\mathrm{d}^{n-j} X}{\mathrm{d}\beta^{n-j}}.$$

We only have to calculate the result at $\beta = 0$ using $X(0) = 1$ and collect on the left-hand side the highest order derivative. In particular, (3.8) gives the first derivative $\mathrm{d}X(0)/\mathrm{d}\beta = -\alpha/(1-\alpha)$. Eq. (3.6b) immediately stems from (3.4), while (3.6c) is due to the obvious identification $c_n(\alpha) = \mathrm{d}^n X/\mathrm{d}\beta^n(0)$ in (3.6a). □

The lower-order derivatives $\mathrm{d}^n X/\mathrm{d}\beta^n(0)$ can also be simply reckoned in an explicit way, so leading to a useful formula for $\zeta(\beta)$ at small β.

Proposition 10. *For any* $\alpha \in (0, 1)$, *the following relationships hold:*

$$\text{(i)} \quad \frac{\mathrm{d}X}{\mathrm{d}\beta}(0) = -\frac{\alpha}{1-\alpha}; \tag{3.9a}$$

$$\text{(ii)} \quad \frac{\mathrm{d}^2X}{\mathrm{d}\beta^2}(0) = \alpha\frac{1+\alpha-\alpha^2}{(1-\alpha)^3}; \tag{3.9b}$$

$$\text{(iii)} \quad \sum_{k=1}^{\infty}\frac{k^{k-1}}{k!}(\alpha e^{-\alpha})^{k-1}(k-1) = \frac{\alpha}{1-\alpha}e^{\alpha}; \tag{3.9c}$$

$$\text{(iv)} \quad \sum_{k=1}^{\infty}\frac{k^{k-1}}{k!}(\alpha e^{-\alpha})^{k-1}(k-1)^2 = \alpha\frac{1+\alpha-\alpha^2}{(1-\alpha)^3}e^{\alpha}; \tag{3.9d}$$

$$\text{(v)} \quad \zeta(\beta) = e^{-\beta}\left[1-\frac{\alpha}{1-\alpha}\beta+\alpha\frac{1+\alpha-\alpha^2}{2(1-\alpha)^3}\beta^2+O(\beta^3)\right] \quad (\beta\to 0). \tag{3.9e}$$

Proof. Relationships (3.9a)–(3.9d) immediately follow from (3.6), whereas (3.9e) is a truncation of (3.3) in Proposition 8. □

As a conclusion, by the previous proposition, for $\alpha \in (0, 1)$ and $\beta \sim 0$ the corrected form of the Kelvin equation is

$$\frac{P_v}{P_0} = e^{-\beta}\left[1-\frac{\alpha}{1-\alpha}\beta+\alpha\frac{1+\alpha-\alpha^2}{2(1-\alpha)^3}\beta^2+O(\beta^3)\right]$$

where the parameters α and β are defined according to (2.2).

4. Conclusions

The complete form of the Kelvin equation, which accounts for the effect of interface curvature on the equilibrium vapour pressure in the presence of the corresponding liquid has been investigated, paying particular attention to the problems of the existence and regularity of solutions. A rigorous power series expansion of the physically meaningful solution has been derived by using Lagrange's expansion. The problem of the convergence of the appropriate algorithm for numerical estimates, concerning in particular the exponential rate and uniformity of the convergence, has also been addressed. Noticeably, the same results can also be applied to the more realistic situation of multicomponent liquid–vapour systems, for a vapour phase of given composition, under the reasonable assumption that the vapour phase can be treated as a mixture of perfect gases. In such a case, indeed, it is easy to prove [2,3] that the generalized Kelvin equation takes a form analogous to (1.2), provided that the molar concentration $1/v_\ell$ of the unique component in the liquid phase of the one-component system is replaced with the total molar concentration C of the liquid phase in the multicomponent system

$$P_v - P_0 - RTC\ln\left(\frac{P_v}{P_0}\right) = 2\gamma H, \tag{4.1}$$

C being the sum of the molar concentrations of each component in the liquid phase. As a consequence, the same formulas established throughout the paper can be applied by considering the parameters

$$\alpha = \frac{P_0}{RTC} \in \mathbb{R}^+ \qquad \beta = \frac{2\gamma H}{RTC} \in \mathbb{R} \tag{4.2}$$

instead of (2.2).

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