

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.

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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]

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

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

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

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

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

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

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

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

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

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.

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