Comments

Comment on Is a Sessile Drop in an Atmosphere Saturated with Its Vapor Really at Equilibrium?

In a recent Letter,[1] M. E. R. Shanahan concludes that a droplet of a liquid on a substrate, in an atmosphere saturated in the vapor of the liquid cannot be at equilibrium. According to ref 1 this is the case because the pressure p of the saturated vapor, given by the Kelvin equation

$$\ln\left(\frac{p}{p_0}\right) = \frac{2\gamma v}{k_B T a} \qquad (1)$$

depends on the curvature $C = a/2$ of the drop and consequently of the height z (γ is the surface tension; here v is the molecular volume k_B the Boltzmann constant, T the temperature, p_0 the vapor pressure above a plane surface of the liquid in question). The curvature of the drop, $C(z)$, is given by Laplace's equation, expressing the mechanical equilibrium of the liquid drop

$$\gamma C(z) = \frac{2\gamma}{b} + \Delta\rho g z \qquad (2)$$

where b is the radius of curvature of the droplet at its highest point, $\Delta\rho$ is the density difference between the liquid and the vapor, g is the gravitational acceleration.

By substituting the curvature $C(z)$ from eq 2 into eq 1, the author concludes that the equilibrium vapor pressure p should also become a function of z. This leads to the surprising conclusion that the drop evaporates at a height for which the curvature is relatively large (close to the substrate) and the vapor condenses at the z level where the curvature is relatively small, i.e., close to the top of the drop. This is a very striking conclusion indeed, because as a consequence the system behaves as a motor that produces mechanical energy without any source of energy! A flux of vapor around the drop and a flux of liquid in the drop are permanently present in a system at thermal equilibrium. The remark of the author that the flow is very small does not change anything; the system violates the second law of thermodynamics. The introduction of a turbine in the flowing vapor or liquid should produce mechanical energy without any source of energy (Figure 1)! Moreover, the evaporation and condensation would also create (without any source of energy) a temperature gradient, also in contradiction with the second law of thermodynamics.

What is wrong?

The Kelvin equation (eq 1) expresses that vapor and liquid are at equilibrium when their chemical potentials are equal. A variation of pressure inside the drop, due to capillarity, modifies the chemical potential μ of the liquid and consequently the vapor pressure in equilibrium

$$d\mu = -S\, dT + v\, dp$$

(1) Shanahan, M. E. R. *Langmuir* **2002**, *18*, 7763.

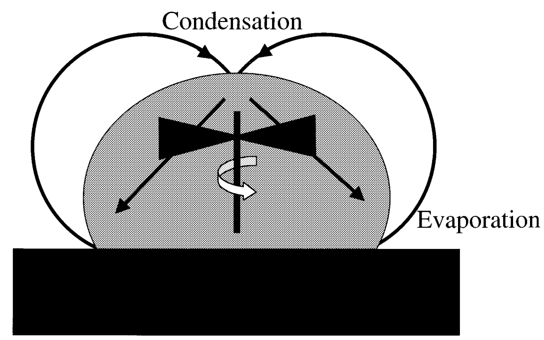

Figure 1. Consequence of the wrong use of the Kelvin's equation: the liquid in a sessile drop and the vapor around the drop flow permanently. The system is a motor that violates the second law of the thermodynamics. A turbine introduced in the drop could produce mechanical energy without source of energy.

where S is the entropy and v the volume per molecule. At constant temperature, $dT = 0$, and $dp = \gamma\, dC$, consequently the variation of μ due to the capillarity is

$$d\mu_C = v\gamma\, dC$$

However, this equation in the form given by the author is established *in the absence* of an external field. In presence of gravity, the chemical potential of the liquid contains a term which is proportional to the external field[2]

$$d\mu_g = -\rho v g\, dz$$

The sum of the two terms $\mu_C + \mu_g$ is constant and equal to $2v\gamma/b$ in the drop. This simply follows from the observation that the chemical potential is uniform within the drop; therefore the chemical potential at the apex of the drop equals, by definition, the chemical potential everywhere in the drop.

The Kelvin equation in the presence of gravity then becomes

$$\ln\left(\frac{p}{p_0}\right) = \frac{v}{k_B T}(\gamma C - \Delta\rho g z) \qquad (3)$$

which shows that the vapor pressure p is independent of the height z. (In this equation the vapor and liquid compressibilities have been neglected for simplicity.) At equilibrium there is no evaporation and no condensation, as one expects intuitively.

(2) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Their Course of Theoretical Physics, Vol. 5; Pergamon Press: London, Paris, 1959; p 72.

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Conclusion

A sessile drop can be perfectly in equilibrium with its vapor. However, as indeed remarked by the author, this is not the case in the presence of a reservoir with a flat liquid surface. It is well known and explained by the Kelvin equation (gravity is not necessary) that when two drops coexist with different radii of curvature, the smaller one evaporates and liquid condenses in the big one.

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