# AN EQUATION FOR THE DENSITY OF A SUBSTANCE IN THE SURFACE LAYER OF LIQUID UNDER ITS OWN SATURATED VAPOR

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An equation is derived for the density of a substance in the surface layer of a liquid under its own saturated vapor, an equation from which expressions can be found for the surface tension and for the thickness of the surface layer. On the basis of irreversible thermodynamic processes, an expression is then also derived for the specific force, per unit mass, acting in the interphase region.

The well-known Fuks equation for the surface tension as given in [1-2], for example, can serve as a basis for deriving an equation for the density of a substance in the interphase layer of a liquid and its own saturated vapor. The Fuks equation is

$$\sigma = \frac{2C_2}{2!}\int_1^2 \rho'^2 dx - \frac{4C_4}{4!}\int_1^2 \rho''^2 dx + \frac{6C_6}{6!}\int_1^2 \rho^{\mathrm{IV}^2} dx - \ldots \tag{1}$$

for a plane interphase boundary. The constants $C_2$ and $C_4$ are

$$C_2 = \int_0^\infty x^2\psi(x)\,dx;\; C_4 = \int_0^\infty x^4\psi(x)\,dx, \quad \psi(x) = 2\pi k\lambda e^{-\frac{x}{\lambda}}. \tag{2}$$

The constant k is related to the constant f in [1]. An analysis has shown that f is the product of constant k and the density of the given substance. It is claimed in [1] that f = 1. It will be shown here that this is not true.

In order to derive an equation for the density of a substance, we will use the first two terms on the right-hand side of Eq. (1).

First we calculate the constants $C_2$ and $C_4$ from Eqs. (2) and the expression for the Laplace function $\psi(x)$. Integration yields

$$C_2 = 4\pi k\lambda^4,\; C_4 = 48\pi k\lambda^6.$$

If the surface layer is at equilibrium (we consider a surface layer with an area of S cm$^2$), then obviously the surface tension $\sigma$ will be minimum. Then

$$\delta\sigma = \int_1^2 \varphi(\rho', \rho'')\,dx = 0, \tag{3}$$

i.e., in this case the first variation of functional (1) will be equal to zero. The Euler equation for functional (1) under condition (3) is (the third term and the terms after the fourth on the right-hand side of (1) are disregarded):

$$\rho'' + 2\lambda^2\rho^{\mathrm{IV}} = 0. \tag{4}$$

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The result here is a linear fourth-order equation with the right-hand side zero. Its solution is

$$\rho = C^{\mathrm{I}} + C^{\mathrm{II}} x + C^{\mathrm{III}} \sin\left(C^{\mathrm{IV}} + \frac{x}{\lambda\sqrt{2}}\right). \tag{5}$$

Here $C^{\mathrm{I}}$, $C^{\mathrm{II}}$, $C^{\mathrm{III}}$, and $C^{\mathrm{IV}}$ are integration constants found from the following boundary conditions: $\rho(1) = \rho_1$, $\rho(2) = \rho_2$, $\rho'(1) = 0$, $\rho'(2) = 0$ (the zero point is taken in the plane of contact between the liquid phase and the gaseous phase, the saturated vapor being regarded here as the gaseous phase). These boundary conditions yield

$$\rho = \rho_1 - l_1 \frac{\rho_1 - \rho_2}{l_1 + l_2} - \frac{\rho_1 - \rho_2}{l_1 + l_2} x + \frac{\lambda\sqrt{2}(\rho_1 - \rho_2)}{l_1 + l_2} \sin\left(\frac{l_1}{\lambda\sqrt{2}} + \frac{x}{\lambda\sqrt{2}}\right). \tag{6}$$

It is necessary to remember here that function (6) must have no extremum but must monotonically decrease on the interval $-l_1$, $l_2$ (the liquid phase is assumed to be on the left-hand side). This is possible only when

$$\lambda = \frac{\Delta L}{2\pi\sqrt{2}}, \text{ i.e., } l_2 = -l_1 + 2\pi\sqrt{2}\lambda. \tag{7}$$

Inserting (6) into (1) and performing the integration, we obtain an equation for the surface tension

$$\sigma = \frac{4\pi k\lambda^4}{\Delta L}(\rho_1 - \rho_2)^2. \tag{8}$$

The thickness of the surface layer is

$$\Delta L = \frac{4\pi k\lambda^4}{\sigma}(\rho_1 - \rho_2)^2. \tag{9}$$

With the aid of the well-known Legendre rule in variational calculus, it is not difficult to establish that, under the given boundary conditions and condition (3), functional (1) has a minimum.

This result is more conveniently checked according to expressions (9) and (7) than according to expressions (8) and (7). First of all, there is no way at this time to determine the exact thickness of a surface layer of any liquid. This thickness is only known to be within $10^{-6}$-$10^{-7}$ cm [3]. Secondly, the exact value of the constant k is also unknown. In [1] f was taken equal to unity, as had been mentioned earlier, but a most elementary calculation will show that this assumption is not justified. Indeed, letting $k = f/\rho$ ($\rho = a$ g/cm$^3$) equal to $1/a$ and calculating $\sigma$ according to formula (8), we obtain values for $\sigma$ which are far from realistic. Much more realistic values are obtained on the assumption that the value of k is close to $(6.02/M) \cdot 10^{23}$ (M denoting the molecular or the atomic weight of the substance comprising the liquid under study).

With the values of surface tension given in [2, 4] for various liquids (water, ethanol, molten metals, liquefied gases, etc.) and with the density $\rho_2$ disregarded, we obtain the thickness of their surface layers as shown in Table 1.

According to Table 1, the calculated thicknesses of the surface layers are closely within the $10^{-6}$-$10^{-7}$ cm range, or slightly outside it. For potassium we list two values for $\Delta$L. The reason for this is that [2] lists two values for $\sigma$. In this author's view, the lower value (in parenthesis) is preferable, since it is close to the thicknesses of the surface layers of other metals related to potassium: sodium and lithium. The calculated values of $\Delta$L probably differ to some extent from the true values, but it also must be remembered that the value of the constant k had been selected intuitively.

The following observation is quite interesting. If all terms after the first one on the right-hand side of the Fuks equation are disregarded (the thus truncated equation is called the Helshof formula), i.e., if the condition is removed which stipulates that the first derivatives $\rho'(-l_1)$ and $\rho'(l_2)$ must vanish, and if the resulting expression is variated, then relation (6) will be replaced by a linear one. In this case, substituting $\rho(x)$ for $\rho$ into the Helshof formula and integrating the result will yield the already known expression (8).

We will now derive an expression for the specific force (F) acting on the substance within the interphase region. For this we use the expression which describes the generalized mass flux J, taken from the

TABLE 1

| Substance | Density of the liquid, $10^{-3}$kg/m$^3$ | Temperature of the liquid | $\sigma \cdot 10^{-3}$. J/m$^2$ | Thickness of the surface layer, cm |
|---|---|---|---|---|
| $He^3$ | 0,0824 | 0 °K | 0,15 | $3{,}8 \cdot 10^{-7}$ |
| $He^4$ | 0,145 | 0 °K | 0,35 | $3.8 \cdot 10^{-7}$ |
| $N_2$ | 0.808 | —196 °C | 8,5 | $6{,}66 \cdot 10^{-7}$ |
| $H_2O$ | 1,00 | 0 °C | 73,2 | $1{,}02 \cdot 10^{-6}$ |
| $CH_3CH_2OH$ | 0,79 | 20 °C | 23,0 | $1{,}12 \cdot 10^{-6}$ |
| Na | 0,928 | 100 °C | 206,4 | $1{,}65 \cdot 10^{-6}$ |
| K | 0,822 | 79 °C | 400,5 (101) | $2{,}7 \cdot 10^{-6}$ ($1{,}68 \cdot 10^{-6}$) |
| Li | 0,507 | 200 °C | 398 | $0{,}96 \cdot 10^{-6}$ |
| Al | 2,44 | 706 °C | 494 | $1{,}22 \cdot 10^{-6}$ |
| Mg | 1,56 | 681 °C | 563 | $1{,}67 \cdot 10^{-6}$ |
| Pb | 10,51 | 400 °C | 438 | $7{,}73 \cdot 10^{-7}$ |
| Sn | 6,72 | 600 °C | 506 | $1{,}02 \cdot 10^{-6}$ |
| Fe | 7,23 | 1530 °C | 1395 | $1{,}07 \cdot 10^{-6}$ |
| Hg | 13,55 | 20 °C | 476 | $7.52 \cdot 10^{-7}$ |
| Au | 17,1 | 1200 °C | 1120 | $8{,}5 \cdot 10^{-7}$ |
| Pt | 18,9 | 2000 °C | 1819 | $0{,}936 \cdot 10^{-7}$ |

thermodynamics of irreversible processes in interphase (liquid–gas) regions [5]. For a liquid in equilibrium with its own vapor, this expression becomes (diffusion due to pressure is disregarded here)

$$J = aX = a\left[F - \left(\frac{\partial\mu}{\partial\rho}\right)_{T,P} \frac{\partial\rho}{\partial x}\right]. \tag{10}$$

For the equilibrium case, the generalized mass flux J is equal to zero and it easily follows from (10) that

$$F = \left(\frac{\partial\mu}{\partial\rho}\right)_{T,P} \frac{\partial\rho}{\partial x} = \left(\frac{\partial\mu}{\partial\rho}\right)_{T,P} \left[\frac{\rho_2 - \rho_1}{\Delta L} + \frac{\rho_1 - \rho_2}{\Delta L} \cos\left(\frac{l_1}{\lambda\sqrt{2}} + \frac{x}{\lambda\sqrt{2}}\right)\right]. \tag{11}$$

In conclusion, we note that the formula for ΔL in [2]

$$\Delta L = A\left(\frac{\rho_1 - \rho_2}{\sigma}\right)^2 \tag{12}$$

does not, in principle, differ from formula (9) derived here.

It was also mentioned in [2] that formula (12) had not been derived rigorously. Formula (9), on the other hand, was derived rigorously and, therefore, is theoretically quite important.

## NOTATION

| | |
|---|---|
| $\sigma$ | is the surface tension, J/m$^2$; |
| $\rho$ | is the density of the substance, kg/m$^3$; |
| $\lambda$ | is a constant which characterizes the drop in force field intensity with increasing distance from the source, cm; |
| f | is a constant, 1/sec$^2$; |
| k | is a constant which characterizes the interaction between two macroparticles due to intermolecular macroforces, m$^3$/kg · sec$^2$; |
| $\delta$ | is the sign of variation; |
| $\rho(1)$, $\rho(2)$ (or alternatively $\rho_1$, $\rho_2$) | are the densities of the substance at the boundary points $l_1$, $l_2$ of the surface layer; |
| $\Delta L = l_1 + l_2$ | is the thickness of the surface layer, cm; |
| F | is the specific force, N/kg; |
| J | is the generalized mass flux, kg/m$^2$ · sec; |
| $a$ | is a phenomenological coefficient; |
| X | is the generalized force; |
| $\mu$ | is the specific chemical potential, J/kg; |
| A | is a constant. |

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