# Droplets and layers in the gradient model of a capillary liquid 

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The gradient model of the capillary liquids recently proposed by the author [1] is employed for the investigation of the equilibrium of the droplets and films with their saturated vapours. The well known dependence of the saturated vapour pressure versus the interfacial curvature is obtained within the framework of the model. A relation between the film tension and the film thickness is derived. Some of these results are employed for the analysis of the stability of the constant density solutions of the equilibrium equation within the regions of the supersaturated vapour and the superheated liquid.

Gradientowy model cieczy kapilarnej, zaproponowany poprzednio przez autora [1], zastosowano do badania równowagi kropel oraz błonek cieczy z ich parą nasyconą. Otrzymano na gruncie tego modelu znaną zależność prężności pary nasyconej od krzywizny powierzchni. Wyprowadzono wzór na zależność napięcia błonki od jej grubości. Część z otrzymanych wyników zastosowano do analizy stateczności rozwiązań o jednorodnej gęstości w obszarze pary przesyconej i cieczy przegrzanej.

Предложенная ранее автором [1] градиентная модель капилярной жидкости используется для анализа равновесия капель и пленок с насыщенным паром. На почве этой модели выводится известная зависимость давления насьщенного пара от кривизны поверхности. Выводится также зависимость натяжения тонкой пленки от ее толщины. Полученные результаты используются для анализа устойчивости решений с однородной плотностью в области пересыщенного пара и перегретой жидкости.

## 1. Introduction

A non-LINear gradient theory was proposed in Ref. [1] for approximate description of liquids with simple non-local interactions. The equation obtained had the form

$$
\begin{equation*}
-\nabla P(\varrho)+\Phi_{3} \varrho \nabla \Delta \varrho=0, \tag{1.1}
\end{equation*}
$$

where

| $\varrho \varrho$ | density, |
| ---: | :--- |
| $P(\varrho)$ | density function, which may be interpreted, for an infinite homogeneous |
|  | medium of constant density, as pressure, |
| $\Phi_{3}$ | material constant characterizing the non-local interactions, |
| $\nabla$ | gradient operator, |
| $\Delta$ | Laplacian operator. |

With an appropriate form of $P(s)$ the Eq. (1.1) has a one-dimensional solution with variable density, which may be interpreted as a model of equilibrium between the liquid phase and the saturated vapour. For such a solution we can determine the surface tension at the interface between the two phases, which is

$$
\begin{equation*}
\sigma=\Phi_{3} \int_{-\infty}^{\infty}\left(\varrho^{\prime}\right)^{2} d x . \tag{1.2}
\end{equation*}
$$

To estimate the share of the gradient term in the Eq. (1.1) a quantity $l$ has been introduced, defined as follows

$$
\begin{equation*}
l \equiv \sqrt{\frac{\Phi_{3} \varrho_{L}}{c^{2}}} \tag{1.3}
\end{equation*}
$$

where $\varrho_{L}$ - the asymptotic value of the density of the liquid (at a considerable distance from the transition zone) and $c^{2}$-the square of the velocity of sound. The estimations made (compare [1]) have shown that $l$ can e.g. be of order $10^{-7} \mathrm{~cm}$.

Although the Eq. (i.1) can be solved in quadratures, accurate determination of $\sigma$ comes up against difficulties of physical nature (some mathematical difficulties can easily be overcome by solving numerically appropriate integrals) consisting in the fact that the function $P(\varrho)$ can be found experimentally, in general, only for certain variability ranges of $\varrho$ corresponding to regions of existence of a stable or metastable solution of constant density.

Thus direct verification of usefulness of the model submitted is difficult.
In the present paper it will be shown that further investigations of the model considered lead to quantitative conclusions in agreement with the classical retations obtained in a different way. It will also be attempted to use the present model for the investigation of those surface problems which cannot be tackled by a two-dimensional mechanical model of the interface.

## 2. Spherically symmetric solutions

It will be assumed that the solution of the Eq. (1.1) is known for the conditions considered in [1], in which we have $\varrho^{\prime} \rightarrow 0, \varrho^{\prime \prime} \rightarrow 0$ for $x \rightarrow \pm \infty$ and the density itself tends to certain finite values, which may be interpreted according to [1] as the density of liquid and saturated vapour.

For a problem of spherical symmetry (i.e. for a droplet or a bubble), the Eq. (1.1) takes the form:

$$
\begin{equation*}
-\frac{\partial P}{\partial \varrho} \varrho^{\prime}+\Phi_{3} \varrho\left(\varrho^{\prime \prime}+\frac{2}{r} \varrho^{\prime}\right)^{\prime}=0 \tag{2.1}
\end{equation*}
$$

(the "prime" denoting differentiation with respect to the radius $r$ ) with the boundary conditions

$$
\begin{array}{lll}
\varrho \rightarrow \varrho_{\infty}, & \varrho^{\prime} \rightarrow 0, & \varrho^{\prime \prime} \rightarrow 0,
\end{array} \quad \text { for } r \rightarrow \infty, ~ 子 \varrho_{0}, \quad \varrho^{\prime} \rightarrow 0, \quad \varrho^{\prime \prime} \rightarrow \varrho_{0}^{\prime \prime}, \quad \text { for } r \rightarrow 0, ~ l
$$

where $\varrho_{o}^{\prime \prime}$ is finite.
If the radius of the droplet (or of the bubble) tends to infinity, the solution of the problem should tend to the solution of the former one-dimensional problem. Let us see now how the values of the density and the pressure of the liquid phase in the droplet and the saturated vapour vary as compared with the limit case of a droplet of infinite radius $\left({ }^{1}\right)$.

[^0]Integration of (2.1) from $r$ to $\infty$ yieds

$$
\begin{equation*}
-\left(P_{\infty}-P(\varrho)\right)-\Phi_{3}\left(\varrho \varrho^{\prime \prime}+\frac{2}{r} \varrho \varrho^{\prime}-\frac{1}{2} \varrho^{\prime 2}\right)-\Phi_{3} \int_{r}^{\infty} \frac{2}{t} \varrho^{\prime 2}(t) d t=0 . \tag{2.2}
\end{equation*}
$$

On multiplying this by $\varrho^{\prime} / \varrho^{2}$ and integrating by parts from $r$ to $\infty$, we obtain

$$
\begin{equation*}
\int_{\varrho}^{\varrho_{\infty}} \frac{P(u)-P_{\infty}}{u^{2}} d u+\frac{1}{2} \Phi_{3} \frac{\varrho^{\prime 2}}{\varrho}-2 \Phi_{3} \frac{1}{\varrho} \int_{r}^{\infty} \frac{1}{t} \varrho^{\prime 2}(t) d t=0 . \tag{2.3}
\end{equation*}
$$

If we let $\frac{2}{r} \varrho \varrho^{\prime}$ tend to the limit for $r=0$, then, on eliminating the indeterminateness, we have

$$
\begin{equation*}
\lim _{r \rightarrow 0} \frac{2}{r} \varrho \varrho^{\prime}=2 \varrho_{0} \varrho_{0}^{\prime \prime} \tag{2.4}
\end{equation*}
$$

therefore (2.2) and (2.3) take, for $r=0$, the form:

$$
\begin{align*}
& P_{0}-P_{\infty}-2 \Phi_{3} \int_{0}^{\infty} \frac{1}{r} \varrho^{\prime 2} d r-3 \Phi_{3} \varrho_{0} \varrho_{0}^{\prime \prime}=0  \tag{2.5}\\
& \int_{\varrho_{0}}^{\varrho_{\infty}} \frac{P(\varrho)-P_{\infty}}{\varrho^{2}} d \varrho-2 \Phi_{3} \frac{1}{\varrho_{0}} \int_{0}^{\infty} \frac{1}{r} \varrho^{\prime 2} d r=0
\end{align*}
$$

It will be shown later for a droplet of radius $R \gg 1$ that the last term of the Eq. (2.5) may be represented in the form:

$$
\begin{equation*}
3 \Phi_{3} \varrho_{0} \varrho_{0}^{\prime \prime}=-\frac{\varrho_{0} k c^{2}}{\frac{l}{R} \operatorname{sh} \frac{R}{l}-1}, \tag{2.7}
\end{equation*}
$$

where $k$ is some constant which will be defined later. With this assumption and bearing in mind that the thickness of the transition layer is small in practice as compared with $R$, we can assume that $\sigma$ practically does not depend on $R$ and can be expressed as in (2.1), and that the second integral in (2.5) and (2.6) can be replaced by $\sigma / R$, i.e.:

$$
\Phi_{3} \int_{0}^{\infty} \varrho^{\prime 2} d r \approx \sigma \approx \mathrm{const}
$$

$$
\begin{equation*}
\Phi_{3} \int_{0}^{\infty} \frac{1}{r} \varrho^{\prime 2} d r \approx \frac{\sigma}{R} \tag{2.8}
\end{equation*}
$$

( $R$ may be, for instance, the radius corresponding to maximum value of $\varrho^{\prime 2}$ ).

[^1]Then, we can write

$$
\begin{equation*}
P_{0}-P_{\infty}-2 \frac{\sigma}{R}+\varrho_{0} \frac{k c^{2}}{\frac{I}{R} \operatorname{sh} \frac{R}{l}-1}=0 \tag{2.9}
\end{equation*}
$$

$$
\begin{equation*}
\int_{\varrho_{0}}^{\varrho_{\infty}} \frac{P(\varrho)-P_{\infty}}{\varrho^{2}} d \varrho-\frac{1}{\varrho} 2 \frac{\sigma}{R}=0 \tag{2.10}
\end{equation*}
$$

Let us denote for convenience $\varrho_{0} \equiv y, \varrho_{\infty} \equiv z, \frac{1}{R} \equiv x$ and express (2.9) in the form $F(x, y, z)=0$ and (2.10) in the form $\Phi(x, y, z)=0$. Use will now be made of the relation

$$
\begin{equation*}
\frac{d z}{d x}=\frac{F_{x}^{\prime} \Phi_{y}^{\prime}-F_{y}^{\prime} \Phi_{x}^{\prime}}{F_{y}^{\prime} \Phi_{z}^{\prime}-F_{x}^{\prime} \Phi_{y}^{\prime}} . \tag{2.11}
\end{equation*}
$$

By calculating the relevant derivatives and finding the limit for $1 / R \rightarrow 0$, we obtain

$$
\begin{equation*}
\frac{d \varrho_{\infty}}{d\left(\frac{1}{R}\right)}=\frac{2 \sigma}{\left.\frac{\partial P}{\partial \varrho}\right|_{\varrho=\varrho_{G}}} \cdot \frac{1}{\left(\frac{\varrho_{L}}{\varrho_{G}}-1\right)} \tag{2.12}
\end{equation*}
$$

or

$$
\begin{equation*}
\frac{d P\left(\varrho_{\infty}\right)}{d\left(\frac{1}{R}\right)}=2 \sigma \frac{1}{\frac{\varrho_{L}}{\varrho_{G}}-1} \tag{2.13}
\end{equation*}
$$

where $\varrho_{L}, \varrho_{G}$ are the densities of the liquid and the saturated vapour for $R \rightarrow \infty$, respectively. Then, bearing in mind that $\varrho_{L}>\varrho_{G}$, we obtain, as an approximation (linear in $1 / R)$ the following equation for the pressure of saturated vapour $P_{s}^{(R)}$ in equilibrium with a droplet of radius $R$ :

$$
\begin{equation*}
P_{s}^{(R)} \approx P_{s}^{\infty}+\frac{\varrho_{G}}{\varrho_{L}} \frac{2 \sigma}{R} \tag{2.14}
\end{equation*}
$$

where $P_{s}^{\infty}$ is the pressure of saturated vapour in equilibrium with a plane surface. From similar considerations we obtain for the pressure at the centre of a vapour bubble of radius $r$

$$
\begin{equation*}
P_{s}^{(r)} \approx P_{s}^{\infty}-\frac{\varrho_{G}}{\varrho_{L}} \frac{2 \sigma}{R} \tag{2.15}
\end{equation*}
$$

It remains to verify the approximate equation (2.7). For $R \gg 1$ the density gradient in the inner region of the droplet is small, it can therefore be assumed that $\partial P / \partial \rho=c^{2}=$ $=$ const. Thus, on dividing by $\varrho$ and integrating, we can write the equation of equilibrium (2.1) in the following form:

$$
\begin{equation*}
-c^{2} \ln \frac{\varrho}{\varrho_{0}}+\Phi_{3}\left(\varrho^{\prime \prime}-\frac{2}{r} \varrho^{\prime}\right)-3 \Phi_{3} \varrho_{0}^{\prime \prime}=0 \tag{2.16}
\end{equation*}
$$

On introducing the symbol $\alpha \equiv\left(\varrho_{0}-\varrho\right) / \varrho_{0}[\alpha \ll 1]$ and making use of (1.3) we find the equation

$$
\begin{equation*}
\frac{1}{l^{2}}\left[\ln (1-\alpha)+3 l^{2} \frac{\varrho_{0}^{\prime \prime}}{\varrho_{0}}\right]+\alpha^{\prime \prime}+\frac{2}{r} \alpha^{\prime}=0 \tag{2.17}
\end{equation*}
$$

On linearizing with respect to $\alpha(\ln (1-\alpha) \approx-\alpha)$ and substituting

$$
\begin{equation*}
y \equiv r\left(3 l^{2} \frac{\varrho_{0}^{\prime \prime}}{\varrho_{0}}-\alpha\right), \tag{2.18}
\end{equation*}
$$

we obtain

$$
\begin{equation*}
y^{\prime \prime}-\frac{1}{l^{2}} y=0 \tag{2.19}
\end{equation*}
$$

Solving this with the conditions

$$
\varrho(0)=\varrho_{0}<\infty,\left|\varrho_{0}^{\prime \prime}\right|<\infty,
$$

we find

$$
\begin{equation*}
\varrho=\varrho_{0}+3 l^{2} \varrho_{0}^{\prime \prime}\left(\frac{l}{r} \operatorname{sh} \frac{r}{l}-1\right) \tag{2.20}
\end{equation*}
$$

The approximations used give a good result for $\left(\varrho_{0}-\varrho\right) / \varrho_{0} \ll 1$ only, therefore we cannot make use of the conditions at infinity and there remains a free parameter $\varrho_{0}^{\prime \prime}$.

It is known, however, that the gradient zone is usually very narrow and the gradient is very steep, we can assume therefore for the radius of the droplet a certain value $r=R$, for which $\left(\varrho_{0}-\varrho\right) / \varrho_{0}=k$, where $0<k<\left(\varrho_{0}-\varrho_{\infty}\right) / \varrho_{0}$ is (to some extent arbitrary) constant determining the boundary of the liquid phase. Then, from (2.20) we obtain

$$
\begin{equation*}
\varrho_{0}^{\prime \prime}=-\frac{\varrho_{0} k}{3 l^{2}} \frac{1}{\frac{l}{R} \operatorname{sh} \frac{R}{l}-1} . \tag{2.21}
\end{equation*}
$$

Hence (2.7).

## 3. Solution for a symmetric layer

In the same manner as was done in the foregoing section for a droplet we can confront the solution for the finite layer with the asymptotic solution for a layer of infinite thickness. In the one-dimensional problem the equation of equilibrium has the form:

$$
\begin{equation*}
-\frac{\partial P}{\partial \varrho} \varrho^{\prime}+\Phi_{3} \varrho \varrho^{\prime \prime \prime}=0 . \tag{3.1}
\end{equation*}
$$

The problem will be considered, with the same boundary conditions, for the interval $0 \leqslant x \leqslant \infty$, in a manner similar to the above. Thus, we have on integrating

$$
\begin{equation*}
-\left(P(\varrho)-P\left(\varrho_{0}\right)\right)+\Phi_{3}\left(\varrho \varrho^{\prime \prime}-\frac{1}{2} \varrho^{\prime 2}\right)-\Phi_{3} \varrho_{0} \varrho_{0}^{\prime \prime}=0, \tag{3.2}
\end{equation*}
$$

and

$$
\begin{equation*}
\int_{\varrho_{0}}^{\varrho} \frac{P(u)-\left[P\left(\varrho_{0}\right)-\Phi_{3} \varrho_{0} \varrho_{0}^{\prime \prime}\right]}{u^{2}} d u+\frac{1}{2} \Phi_{3} \frac{\varrho^{\prime 2}}{\varrho}=0 . \tag{3.3}
\end{equation*}
$$

For $\varrho=\varrho_{\infty}$ we obtain

$$
\begin{align*}
& \boldsymbol{P}_{0}-\boldsymbol{P}_{\infty}-\Phi_{3} \varrho_{0} \varrho_{0}^{\prime \prime}=0,  \tag{3.4}\\
& \int_{e_{0}}^{e_{\infty}} \frac{P(u)-P\left(\varrho_{\infty}\right)}{u^{2}} d u=0 .
\end{align*}
$$

The functions (3.4) and (3.5) will be considered as functions of three variables: $\varrho_{0}, \varrho_{\infty}$ and $\varrho_{0}^{\prime \prime}$. On denoting in an appropriate manner the variables and applying equations of the type (2.11), we obtain

$$
\begin{equation*}
\left.\frac{d \varrho_{0}}{d\left(\varrho_{0}^{\prime \prime}\right)}\right|_{\varrho=0}=l^{2},\left.\quad \frac{d \varrho_{\infty}}{d\left(\varrho_{0}^{\prime \prime}\right)}\right|_{\varrho_{0}^{\prime \prime}=0}=0 . \tag{3.6}
\end{equation*}
$$

With the following definition of the surface tension, similar to [1],

$$
\begin{equation*}
\sigma=\int_{0}^{\infty}\left(T_{y y}-\frac{1}{3} \operatorname{tr} \mathrm{~T}_{\infty}\right) d x \tag{3.7}
\end{equation*}
$$

where $\mathbf{T}=\left(-P+\frac{1}{2} \Phi_{3} \nabla \varrho \cdot \nabla \varrho+\Phi_{3} \varrho \Delta \varrho\right) 1-\Phi_{2} \nabla \varrho \otimes \nabla \varrho$ is a stress tensor, and with the same argument as in [1], we obtain for the case considered

$$
\begin{equation*}
\boldsymbol{\sigma}=\Phi_{3} \int_{0}^{\infty} \varrho^{\prime 2} d x \tag{3.8}
\end{equation*}
$$

From (3.8) and (3.3) we easily find

$$
\begin{equation*}
\sigma=\sqrt{2 \Phi_{3}} \int_{e_{0}}^{e_{\infty}} \sqrt{\varrho \int_{\varrho_{0}}^{\varrho} \frac{P(u)-P\left(\varrho_{\infty}\right)}{u^{2}} d u} d \varrho . \tag{3.9}
\end{equation*}
$$

If $\sigma$ is considered as a function of $\varrho_{0}^{\prime \prime}$, we find

$$
\begin{equation*}
\frac{d \sigma}{d\left(\varrho_{0}^{\prime \prime}\right)}=\frac{\partial \sigma}{\partial\left(\varrho_{0}^{\prime \prime}\right)}+\frac{\partial \sigma}{\partial \varrho_{\infty}} \frac{d \varrho_{\infty}}{d\left(\varrho_{0}^{\prime \prime}\right)}+\frac{\partial \sigma}{\partial \varrho_{0}} \frac{d \varrho_{0}}{d\left(\varrho_{0}^{\prime \prime}\right)} \tag{3.10}
\end{equation*}
$$

On differentiating (3.9), we obtain
$\frac{d \sigma}{d\left(\varrho_{0}^{\prime \prime}\right)}=\frac{\Phi_{3}^{2}}{\varrho_{\infty}} \frac{\sqrt{2 \Phi_{3}} \Phi_{3}^{2} \varrho_{0}^{\prime \prime}}{\left(\frac{1}{\varrho_{\infty}}-\frac{1}{\varrho_{0}}\right)\left(-\left.\frac{\partial P(\varrho)}{\partial \varrho}\right|_{\varrho=थ_{0}}+\Phi_{3} \varrho_{0}^{\prime \prime}\right)+\Phi_{3} \frac{\varrho_{0}^{\prime \prime}}{\varrho_{\infty}} \int_{\varrho_{0}}^{\varrho_{\infty}} \frac{\varrho-\varrho_{\infty}}{\int_{\varrho_{0}}^{\rho} \frac{P(u)-P\left(\varrho_{\infty}\right)}{u^{2}}} d u} d \varrho$.

Now finding $\varrho^{\prime}$ from (3.3) and integrating with respect to $\boldsymbol{x}$, we obtain
(3.12) $\frac{d \sigma}{d\left(\varrho_{0}^{\prime \prime}\right)}=\frac{2 \Phi_{3}^{2} \varrho_{0}^{\prime \prime}}{\varrho_{\infty}\left[\left(\frac{1}{\varrho_{\infty}}-\frac{1}{\varrho_{0}}\right)\left(-\left.\frac{\partial P(\varrho)}{\partial \varrho}\right|_{\varrho=\varrho_{0}}+\Phi_{3} \rho_{0}^{\prime \prime}\right)+\Phi_{3} \frac{\varrho_{0}^{\prime \prime}}{\varrho_{\infty}}\right]} \int_{0}^{\infty}\left(\varrho(x)-\varrho_{\infty}\right) d x$.

The limit for $\varrho_{0}^{\prime \prime} \rightarrow 0$ in (3.12) is connected with an indeterminateness of the type $0 \cdot \infty$, because the integral in the right-hand term is half the "surplus" mass per unit area of the layer, which tends to infinity with the thickness of the layer (for $\varrho_{0}^{\prime \prime} \rightarrow \mathbf{0}$ ). For sufficiently large $x$ and under the conditions

$$
\lim _{x \rightarrow \infty} \varrho=\varrho_{\infty}, \quad \lim _{x \rightarrow \infty} \varrho^{\prime}=0, \quad \lim _{x \rightarrow \infty} \varrho^{\prime \prime}=0
$$

we have $\left(\varrho-\varrho_{\infty}\right) / \varrho_{\infty} \ll 1$ and the Eq. (3.1) can be approximated by the equation

$$
\begin{equation*}
-\left.\frac{\partial P}{\partial \varrho}\right|_{\varrho=\varrho_{\infty}} \varrho^{\prime}+\Phi_{3} \varrho_{\infty} \varrho^{\prime \prime \prime}=0 \tag{3.13}
\end{equation*}
$$

with the same conditions at infinity. A solution of (3.13) is

$$
\begin{equation*}
\varrho=\varrho_{\infty}+C \exp \left(-\sqrt{\left.\frac{\Phi_{3} \varrho_{\infty}}{\left.\frac{\partial P}{\partial \varrho}\right|_{e=e_{\infty}}} x\right), ~, ~, ~, ~}\right. \tag{3.14}
\end{equation*}
$$

where $C$ is the integration constant. It is seen that the integral in (3.12) is convergent at infinity, therefore it suffices to analyse $\lim _{d \rightarrow \infty} \varrho_{0}^{\prime \prime} \int_{0}^{d / 2}\left(\varrho-\varrho_{\infty}\right) d x$, where

$$
\lim _{d \rightarrow \infty} \varrho_{0}^{\prime \prime} \int_{0}^{d / 2}\left(\varrho-\varrho_{\infty}\right) d x<\lim _{d \rightarrow \infty} \varrho_{0}^{\prime \prime} \frac{d}{2}\left(\varrho_{0}-\varrho_{\infty}\right)
$$

The Eq. (3.1) can be approximated inside the layer by

$$
\begin{equation*}
-c^{2} \varrho^{\prime}+\Phi_{3} \varrho \varrho^{\prime \prime \prime}=0 \tag{3.15}
\end{equation*}
$$

On introducing the notations

$$
\begin{equation*}
\alpha \equiv \frac{\varrho_{0}-\varrho}{\varrho_{0}} \tag{3.16}
\end{equation*}
$$

double integration yields

$$
\begin{equation*}
\int_{0}^{\alpha} \frac{t+l^{2} \alpha_{0}^{\prime \prime}}{(1-t)^{2}} d t=\frac{1}{2} l^{2} \frac{\alpha^{\prime 2}}{1-\alpha} \tag{3.17}
\end{equation*}
$$

By evaluating the integral, expanding $\ln (1-\alpha)$ in series and confining ourselves to terms containing $\alpha$ to a power not higher than two, we obtain

$$
\begin{equation*}
l^{2} \alpha^{\prime 2}=2 l^{2} \alpha_{0}^{\prime \prime} \alpha+\alpha^{2} \tag{3.18}
\end{equation*}
$$

This equation can be solved for $x$. The same argument as in the foregoing section leads to the relation

$$
\begin{equation*}
d=4 l \operatorname{Arsh} \sqrt{\frac{k}{2 l^{2} \alpha_{0}^{\prime \prime}}} \tag{3.19}
\end{equation*}
$$

Hence

$$
\begin{equation*}
\varrho_{o}^{\prime \prime}=-\frac{\varrho_{0} k}{2 l^{2}} \frac{1}{\operatorname{sh}^{2} \frac{d}{4 l}} \tag{3.20}
\end{equation*}
$$

Similarly to the foregoing section, the value of $d$ depends on the choice of the limit value for $k$. However, on substituting (3.20) into (3.12) and taking into consideration (3.14) and (3.15), we obtain, irrespective of the values od $d$ and $k$

$$
\begin{equation*}
\lim _{e_{0}^{\prime \prime} \rightarrow 0} \frac{d \sigma}{d\left(\varrho_{0}^{\prime \prime}\right)}=0 \tag{3.21}
\end{equation*}
$$

From (3.21) and (3.6) we find, therefore, for the linear approximation of the parameter $\varrho_{0}^{\prime \prime}$, which is connected with $d$ by the relation (3.20), that $\varrho_{\infty}$ (therefore also $P_{\infty}$ ) and $\sigma$ are independent of $d$. For $\varrho_{0}$ we obtain from (3.6) and (3.20)

$$
\begin{equation*}
\varrho_{0} \approx \varrho_{1}\left(1-\frac{k}{2 \operatorname{sh}^{2} \frac{d}{4 l}}\right) \tag{3.22}
\end{equation*}
$$

As a result of the arbitrariness of the parameter $k$, this equation gives only a rough approximation to $\varrho_{0}$.

The second derivative of $\varrho_{\infty}$ with respect to the parameter $\varrho_{0}^{\prime \prime}$ can easily be found. Then, the next approximation is obtained

$$
\begin{equation*}
\varrho_{\infty} \approx \varrho_{G}\left(1+\frac{1}{8} \frac{c^{2} k^{2}}{\left.\frac{\partial P}{\partial \varrho}\right|_{\varrho=\varrho_{G}} \operatorname{sh}^{4} \frac{d}{4 l}}\right) \tag{3.23}
\end{equation*}
$$

A similar argument for $\sigma$ would be very tedious due to the indeterminatenesses involved in the process of finding the limit. We shall proceed in another way, by treating the expression (3.12) as a differential equation for $\sigma$ in function of $\varrho_{0}^{\prime \prime}$, by linearizing the factor before the integral in $\varrho_{0}^{\prime \prime}$ and applying the approximate equation

$$
\begin{equation*}
\frac{\int_{0}^{\infty}\left(\varrho(x)-\varrho_{\infty}\right) d x}{1-\frac{\varrho_{G}}{\varrho_{L}}} \approx \frac{\varrho_{L} d}{2} \tag{3.24}
\end{equation*}
$$

We obtain the equation

$$
\begin{equation*}
\frac{d \sigma}{d\left(\varrho_{0}^{\prime \prime}\right)}=-\Phi_{3} l^{2} \varrho_{0}^{\prime \prime} d \tag{3.25}
\end{equation*}
$$

where $d$ is a function of $\varrho_{o}^{\prime \prime}$. On changing the variable for $d$, we have

$$
\begin{equation*}
\sigma_{d}^{\prime}=\frac{c^{2} \varrho_{0}}{8 l} k^{2} \frac{\operatorname{ch} \frac{d}{4 l}}{\operatorname{sh}^{5} \frac{d}{4 l}} d \tag{3.26}
\end{equation*}
$$

On integrating (3.26), rejecting terms containing powers of $\frac{1}{\text { sh } d / 4 l}$ higher than the fourth power and denoting by $A(d)$ the tension of a layer of thickness $d$, we obtain

$$
\begin{equation*}
A(d) \approx 2 \sigma_{\infty}-c^{2} \varrho_{0} \frac{k^{2}}{4} \frac{d}{\operatorname{sh}^{4} \frac{d}{4 l}} \tag{3.27}
\end{equation*}
$$

where $\sigma_{\infty}$ is the surface tension for $d \rightarrow \infty$.

## 4. Discussion of results and conclusions

The Eqs. (2.14) and (2.15) for the pressure of saturated vapour in equilibrium with a spherical surface are familiar approximate equations usually derived from the membrane model of the surface on the basis of the second law of thermodynamics (cf. [2]). Using the present model, they have been obtained by purely mechanical considerations. In the present author's opinion this is an additional fact confirming the applicability of the model and the correctness of the method. The same model and the same method applied to the problem of a layer (a film) lead to the Eqs. (3.22) and (3.23) for the density inside the film and the density of saturated vapour in equlibrium with the film. It is easy to obtain the following equation expressing the pressure $P_{g}^{d}$ in equilibrium with a film of thickness $d$ :

$$
\begin{equation*}
P_{s}^{d}=P_{s}^{\infty}+\frac{\varrho_{G} c^{2} k^{2}}{4 \operatorname{sh}^{4} \frac{d}{4 l}} . \tag{4.1}
\end{equation*}
$$

Another equation obtained is the Eq. (3.27) for the membrane tension. These equations cannot be derived from the simple film model of a surface. It remains to observe that the approximation $d \gg l$ was used, which is a "thick film" approximation in the sense of [3], so that, for instance, the apparent paradox of negative density in the Eq. (3.22) for small $d$ has no physical interpretation and is simply a result of a formula being used beyond its applicability range.

Let us observe also that the case studied in Sec. 3 is of no direct practical applicability, the object of the considerations being a film in equilibrium with its saturated vapour only, which would probably be very difficult for experimental realization, but the results obtained show the qualitative effect of surface tension decreasing as a result of a reduction of the linear dimensions and an increase in pressure of saturated vapour. This enables us to suppose, that the case of a drop, for instance, is similar, that is it enables us to expect that the scale effect does not suppress but perhaps strengthens, in the case of very small
drops, "the effect of geometrical form" as expressed by the Eq. (2.14). It can also be expected that the values of pressure, density and energy will remain within reasonable limits even for very small drops, while the membrane model of constant tension leads for $R \rightarrow 0$ to an infinite energy density of the disintegrated medium.

The problem of stability of solutions for constant density was not studied in Ref. [1]. Physical observation show that homogeneous states are instable or quasi-stable within the interval $\varrho_{G}<\varrho<\varrho_{L}$. The case of Region II (Fig. 1), where $\partial P / \partial \varrho<0$, is relatively simple. (The condition of existence of such a region is necessary for the existence of a solution in the case of equilibrium of phases because in the opposite case the condition (3.5), for


Fig. 1.
instance, could not be satisfied). Let us consider a small deviation from the state of equilibrium $u(x)$ within the range of negative $\partial P / \partial \varrho$.

By rejecting non-linear terms we obtain, for a certain density $\varrho^{*}$ in that region,

$$
\begin{equation*}
-\left.\frac{\partial P}{\partial \varrho}\right|_{\varrho=\varrho^{*}} \varrho^{\prime}+\Phi_{3} \varrho^{*} \varrho^{\prime \prime \prime}=\varrho^{*} \ddot{u} . \tag{4.2}
\end{equation*}
$$

Let us consider the displacement field in the direction $x$ from the state of homogeneous $\varrho^{*}$ in the form

$$
\begin{equation*}
u=f(t) \sin \frac{x}{b} \tag{4.3}
\end{equation*}
$$

where $f(t) \ll b$ is a function of time $t$. Then, we have for the density

$$
\begin{equation*}
\varrho=\varrho^{*}\left(1-f(t) \frac{1}{b} \cos \frac{x}{b}\right) \tag{4.4}
\end{equation*}
$$

On substituting (4.3) and (4.4) into (4.2) and integrating (4.2) with respect to time with the boundary conditions $f(0)=a$ and $f^{\prime}(0)=0$, we obtain for $b^{2}>-\frac{\Phi_{3} \varrho^{*}}{\left.\frac{\partial P}{\partial \varrho}\right|_{\varrho=\varrho^{*}}}$
the expression

$$
\begin{equation*}
f(t)=a \operatorname{ch}\left(\frac{b t}{\sqrt{-\left.\frac{\partial P}{\partial \varrho}\right|_{e=e^{*}}-\frac{\Phi_{3} \varrho^{*}}{b^{2}}}}\right) . \tag{4.5}
\end{equation*}
$$

We have therefore an almost exponential growth of the amplitude of small perturbation that is local instability of the solution with constant density $\varrho^{*}$ for any periodic perturbation with a "vawelength" $\lambda>2 \pi \sqrt{\frac{\Phi_{3} \varrho^{*}}{-\left.\frac{\partial P}{\partial \varrho}\right|^{2}=\varrho^{*}}}$. For the considerations of stability, in the regions I and III of saturated vapour and superheated liquid, respectively, the Eqs. (2.14) and (2.15) obtained within the frames of the model considered may be applied. Let us quote the standard argument of the theory of phase processes. It may be assumed, for instance, that we are concerned with homogeneous density $\varrho^{*}>\varrho_{\mathrm{G}}$ in Region I, the corresponding pressure being $P\left(\varrho^{*}\right)>P_{s}$. From the Eq. (2.14) it is seen immediately that the equivalent pressure of saturated vapour for any droplet of diameter $R>R_{K}=$ $=\frac{2 \varrho}{P\left(\varrho^{*}\right)-P_{S}} \frac{\varrho_{G}}{\varrho_{L}}$ is lower than the pressure $P\left(\varrho^{*}\right)$. This means that if there occurs due to any reason, a droplet of radius greater than $R_{k}$, it becomes a nucleus of condensation of the surrounding vapour. The case of Region II is analogous. Any vapour bubble of radius exceeding a certain critical value will grow. This mechanism is well known, of course, but it is only by obtaining (2.14) and (2.15) by analysis of the model itself that it is legitimate to use them for the analysis of this particular model. It is seen that the conclusions are in agreement with the behaviour of real systems.

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[^0]:    ${ }^{(1)}$ In the case of the bubble, all considerations are of course "symmetric".

[^1]:    2 Arch. Mech. Stos. nr 6/74

