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On two phenomenological models of capillary phenomena

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THE GRADIENT model of a capillary liquid is shown to yield the classical formulae both for the capillary pressure and for the saturated vapour pressure over a curved interface. This result is obtained as the first approximation and applies to a wide class of interface geometries, under rather general assumptions regarding the energy density as a function of mass density and its gradient.

Wykazuje się, że przy dostatecznie ogólnych założeniach dotyczących postaci funkcji opisującej zależność gęstości energii od gęstości masy i jej gradientu, gradientowy model cieczy kapilarnej prowadzi w pierwszym przybliżeniu do klasycznych wzorów na ciśnienie kapilarne i na zależność ciśnienia pary nasyconej od krzywizny powierzchni rozdziału.

Доказывается, что при достаточно общих предположениях относительно вида функции, определяющей плотность энергии в зависимости от плотности массы и ее градиента, а также относительно геометрии поверхности раздела, градиентная модель капилярной жидкости приводит в первом приближении к классическим формулам для капиллярного давления и для упругости насыщенного пара над искривленной поверхностью.

THE MEMBRANE model of surface tension has proved to be very effective in the theory of capillary phenomena or, more precisely, in the mechanics of those phenomena; this phenomenological model allows for an effective description of a wide class of mechanical phenomena occurring in a liquid with a free surface, e.g. the capillary waves, droplet vibrations and many others. This model will remain for long a basic tool in investigating the mechanical properties of free surfaces what may be exemplified by the nonlinear solutions obtained in our times by CRAPPER [1] and describing the finite amplitude capillary waves. Some attempts were made to construct a more general description developing the fundamental ideas of that model by treating the interface as a two-dimensional continuum, and introducing the viscosity [2] or the dependence of the surface energy on the radius of curvature (shell model) [3]. At the same time, however, attempts were repeated to apply a three-dimensional description in which the non-locality effect producing the capillary phenomena were accounted for, in the first approximation, by introducing the elastic energy as a function of the density gradient (or, more generally, of the second and higher strain gradients). Let us mention the papers by Young, Maxwell, Laplace, Korteweg, Van der Waals, Fuchs (detailed references may be found in [4]); among the more recently published papers let us mention those by MINDLIN [5] and HART [6].

Paper [7] may serve as an example of practical application of the gradient model when the capillary tube dimensions make the problem lie decidedly outside the region of applicability of the classical membrane theory.

The present author showed in papers [8, 9] that in the case of a certain type of simple molecular interactions the gradient theory may serve as an approximate description of non-local interactions.

The first question to be answered in verifying a new theoretical model is whether in the cases which may effectively be described by the classical model, the generalized model leads to the same experimentally verified results.

The fundamental result of the membrane theory is the Laplace formula

$$\Delta p = 2H\sigma, \tag{1}$$

in which σ — surface tension, Δp — pressure difference at both sides of the interface, H — mean curvature of interface.

In papers [8, 11] the present author proved this formula to hold true in certain simple cases also for the gradient theory. The aim of this paper is to demonstrate that the gradient approach yields the Laplace formula (and also other results known from the classical theory of surface phenomena) under considerably less constraining assumptions concerning both the form of the energy density function depending on the mass density gradient, and the form of the interface.

In papers [8, 9, 10] it was shown that in the absence of body forces the condition of equilibrium in the case of the gradient model of a liquid has the same form as in the classical case

$$T_{ij,j} = 0, \tag{2}$$

while $\mathbf{T}$ is expressed by the formula

$$T_{ij} = -\left[\varrho\frac{\partial(\varrho w)}{\partial\varrho} - \varrho w - 2\varrho\left(\frac{\partial(\varrho w)}{\partial I}\varrho_{,k}\right)_{,k}\right]\delta_{ij} - 2\frac{\partial(\varrho w)}{\partial I}\varrho_{,i}\varrho_{,j}. \tag{3}$$

Here ϱ — density, w — energy density (referred to unit mass), and $I \equiv \varrho_{,i}\varrho_{,i}$.

Thus the relation (2) may be written in the form

$$-\left(\frac{\partial(\varrho w)}{\partial\varrho}\right)_{,i} + 2\left(\frac{\partial(\varrho w)}{\partial I}\varrho_{,k}\right)_{,ki} = 0 \tag{4}$$

or

$$-\frac{\partial(\varrho w)}{\partial\varrho} + 2\left(\frac{\partial(\varrho w)}{\partial I}\varrho_{,k}\right)_{,k} = c = \text{const}. \tag{5}$$

By substituting Eq. (5) into Eq. (3) we obtain in the case of equilibrium and in the absence of the body forces

$$T_{ij} = \varrho(w+c)\delta_{ij} - 2\frac{\partial(\varrho w)}{\partial I}\varrho_{,i}\varrho_{,j}. \tag{6}$$

Let us now consider a certain class of solutions of Eq. (5) and, namely, the class at which the surfaces of constant ϱ are also the surfaces of constant I; this class contains the cases of spherical and cylindrical symmetry and, obviously, the plane case. For practical purposes we may confine ourselves to such cases in which the mean curvature of the equal density surface in the gradient zone is small as compared with the reciprocal of the zone thickness (i.e. with $1/h$, h being the apparent thickness of the zone outside which the density gradient is negligibly small). It may be expected then that, the equal density surfaces will virtually always be parallel to each other in the sense of a common normal, i.e. if at a certain surface $\varrho = \text{const}$, then also $|\text{grad}\,\varrho| = \text{const}$, that is $I = \text{const}$.

Let us select such a coordinate system (x_1, x_2, x_3) in which the $I = I_{\max}$ — surface is the $x_3 = s = 0$ surface, and for all regions close to the surface the variable s represents the distance from it (measured along the normal); the remaining two variables x_1, x_2 may be assumed arbitrarily on the surface P provided they remain constant along the normals.

In the coordinate system introduced here Eq. (5) is written in the form

$$(7)\qquad -\frac{\partial(\varrho w)}{\partial\varrho}+4\frac{\partial^2(\varrho w)}{\partial I^2}\varrho''\varrho'^2+2\frac{\partial^2(\varrho w)}{\partial I\partial\varrho}\varrho'^2+2\frac{\partial(\varrho w)}{\partial I}\left(\varrho''+\frac{2H+2Ks}{1+2Hs+Ks^2}\varrho'\right)=c$$

(cf. the Appendix I), where ϱ', ϱ'' denote the derivatives $\partial\varrho/\partial s$ and $\partial^2\varrho/\partial s^2$, respectively; H is the mean curvature of the surface P, and K — the Gaussian curvature.

In this manner the problem is reduced to a one-dimensional problem. Equation (7) is meaningful only for $s < R_1, R_2$, R_1 and R_2 denoting the principal radii of curvature of surface P; however, as it was mentioned before, sufficiently far away from P the gradient of ϱ is negligibly small and hence we can assume that for certain values of $s = a < 0$ and $s = b > 0$,

$$(8)\qquad \varrho'(b)=0,\quad \varrho'(a)=0,\quad \varrho''(a)=0,\quad \varrho''(b)=0.$$

On substituting these relations into Eq. (7) we obtain

$$(9)\qquad -\frac{\partial(\varrho w)}{\partial\varrho}\bigg|_{s=a} = -\frac{\partial(\varrho w)}{\partial\varrho}\bigg|_{s=b} = c.$$

Equation (7) multiplied by ϱ' may be written as

$$(10)\qquad -\left(\frac{\partial(\varrho w)}{\partial\varrho}\right)'+\left(2\frac{\partial(\varrho w)}{\partial I}\varrho'\right)'\varrho'+2\frac{\partial^2(\varrho w)}{\partial I^2}\varrho'\varrho''+2\frac{\partial^2(\varrho w)}{\partial I^2}\varrho'^2\frac{2H+2Ks}{1+2Hs+Ks^2}=c\varrho'.$$

Integration by parts within the interval $\langle a, b\rangle$ and application of the relations (8) yields

$$(11)\qquad \varrho(w+c)\Big|_a^b = 2\int_a^b \frac{\partial(\varrho w)}{\partial I}\varrho'^2\frac{2H+2Ks}{1+2Hs+Ks^2}\,ds.$$

For $\varrho' = 0$, $w = w(\varrho) = \int \frac{p(\varrho)}{\varrho^2}\,d\varrho$. Here $p = p(\varrho)$ — pressure.

Let us observe that

$$(12)\qquad \varrho\frac{\partial(\varrho w)}{\partial\varrho}-\varrho w = \varrho\int\frac{p}{\varrho^2}\,d\varrho+p-\varrho\int\frac{p}{\varrho^2}\,d\varrho = p$$

and hence

$$\varrho(w+c)\Big|_b^a = -\left(\varrho\frac{\partial(\varrho w)}{\partial\varrho}-\varrho w\right)\Big|_a^b = p_b-p_a,$$

$$(13)\qquad p_b-p_a = 2H\int_a^b 2\frac{\partial(\varrho w)}{\partial I}\varrho'^2\frac{1+Ks/H}{1+2Hs+Ks^2}\,ds \approx 2H\int_a^b 2\frac{\partial(\varrho w)}{\partial I}\varrho'^2 ds.$$

It was shown in [8, 11] that the right-hand integral of Eq. (13) for a plane surface may be interpreted as the surface tension; also in the general case on the basis of the definition given, for example, in the paper by RUSANOV [12]

$$\sigma = \int_a^b (T_t - T_n)ds, \tag{14}$$

(where T_t and T_n are the respective tangential and normal stresses), we obtain with the aid of Eq. (6)

$$\sigma = \int_a^b \left\{\varrho(w+c) - \left[\varrho(w+c) - 2\frac{\partial(\varrho w)}{\partial I}\varrho'^2\right]\right\} ds = 2\int_a^b \frac{\partial(\varrho w)}{\partial I}\varrho'^2 ds. \tag{15}$$

Hence Eq. (13) is reduced to the classical Laplace formula in the same approximation in which $\mathrm{grad}\,\varrho \| \mathrm{grad}\, I$, in which the integral discussed is independent of the shape of the surface $I = I_{\max}$, and in which Eq. (13) was derived.

It is shown in [11] that in the case of spherical symmetry a good approximate formula is obtained for the dependence of the saturated vapour pressure over the curved surface on the radius of curvature. The procedure employed there may be transferred, almost without alterations, to the more general case considered here. The expression for $(w\varrho)|_{I=\mathrm{const}}$ is prescribed with the accuracy up to an additive constant; let us select a reference value $\varrho_0 < \varrho_a$, ϱ_a being the saturated vapour density, so that $\varrho_a < \varrho_b$. Then Eq. (9) may be written as

$$\frac{p(\varrho_a)}{\varrho_a} + \int_{\varrho_0}^{\varrho_a} \frac{p(\varrho)}{\varrho^2} d\varrho = \frac{p(\varrho_b)}{\varrho_b} + \int_{\varrho_0}^{\varrho_b} \frac{p(\varrho)}{\varrho^2} d\varrho, \tag{16}$$

that is

$$\frac{p(\varrho_a)}{\varrho_a} - \frac{p(\varrho_b)}{\varrho_b} - \int_{\varrho_a}^{\varrho_b} \frac{p(\varrho)}{\varrho^2} d\varrho = 0 \tag{17}$$

or

$$\int_{\varrho_a}^{\varrho_b} \frac{1}{\varrho} \frac{dp(\varrho)}{d\varrho} d\varrho = 0. \tag{18}$$

The symbol $dp/d\varrho$ denotes $\left.\frac{\partial p(\varrho, I)}{\partial \varrho}\right|_{I=0}$, and from Eq. (13) it follows that

$$p(\varrho_a) - p(\varrho_b) - 2H\sigma = 0. \tag{19}$$

Denoting the expressions (18) and (19) by $F(\varrho_a, \varrho_b, H)$ and $\Phi(\varrho_a, \varrho_b, H)$, respectively, and disregarding the dependence of σ on H, we obtain

$$\begin{aligned} &\frac{\partial F}{\partial H} = 0, \quad \frac{\partial F}{\partial \varrho_b} = \frac{1}{\varrho_b}\left.\frac{dp}{d\varrho}\right|_{\varrho=\varrho_b}, \quad \frac{\partial F}{\partial \varrho_a} = -\frac{1}{\varrho_a}\left.\frac{dp}{d\varrho}\right|_{\varrho=\varrho_a}, \\ &\frac{\partial \Phi}{\partial H} = -2\sigma, \quad \frac{\partial \Phi}{\partial \varrho_a} = \left.\frac{dp}{d\varrho}\right|_{\varrho=\varrho_a}, \quad \frac{\partial \Phi}{\partial \varrho_b} = -\left.\frac{dp}{d\varrho}\right|_{\varrho=\varrho_b}. \end{aligned} \tag{20}$$

The formula for differentiation of implicit functions yields

$$\frac{d\varrho_a}{dH} = \frac{\dfrac{\partial F}{\partial H}\dfrac{\partial \Phi}{\partial \varrho_b} - \dfrac{\partial F}{\partial \varrho_b}\dfrac{\partial \Phi}{\partial H}}{\dfrac{\partial F}{\partial \varrho_b}\dfrac{\partial \Phi}{\partial \varrho_a} - \dfrac{\partial F}{\partial \varrho_a}\dfrac{\partial \Phi}{\partial \varrho_b}}, \tag{21}$$

whence

$$\frac{d\varrho_a}{dH} = \frac{-\dfrac{1}{\varrho_b}\dfrac{dp}{d\varrho}\Big|_{\varrho=\varrho_b} 2\sigma}{\dfrac{1}{\varrho_b}\dfrac{dp}{d\varrho}\Big|_{\varrho=\varrho_b}\dfrac{dp}{d\varrho}\Big|_{\varrho=\varrho_a} - \dfrac{1}{\varrho_a}\dfrac{dp}{d\varrho}\Big|_{\varrho=\varrho_a}\dfrac{dp}{d\varrho}\Big|_{\varrho=\varrho_b}}, \tag{22}$$

that is

$$\frac{d\varrho_a}{dH} = -\frac{2\sigma}{\left(1-\dfrac{\varrho_b}{\varrho_a}\right)\dfrac{dp}{d\varrho}\Big|_{\varrho=\varrho_a}}. \tag{23}$$

Let us denote by $p_a(H)$ the density of saturated vapour at infinity, remaining in equilibrium with the fluid for a given curvature H. Since p_a is almost independent of H, we may write

$$p_a(H) = p_a(H)|_{H=0} + \frac{dp_a(H)}{dH}\Big|_{H=0} H. \tag{24}$$

From Eq. (23) it follows

$$\frac{dp_a}{d\varrho_a}\frac{d\varrho_a}{dH} = -\frac{2\sigma}{1-\varrho_b/\varrho_a} \tag{25}$$

and hence

$$\frac{dp_a}{dH} = -\frac{2\sigma}{1-\varrho_b/\varrho_a}.$$

The value of $\varrho_a(H)$ differs but slightly from $\varrho_a(0)$, so that

$$\frac{dp_a}{dH} \approx -\frac{2\sigma}{1-\varrho_b/\varrho_a}.$$

Finally,

$$p_a(H) = p(H)_{H=0} + \frac{2\sigma}{\varrho_b/\varrho_a - 1} H \approx p_{H=0} + 2H\sigma\frac{\varrho_a}{\varrho_b}. \tag{26}$$

In the same approximation in which the formulae (19), (26) hold true, the maximum gradient surface must obviously be at the same time the surface of equal mean curvatures.

A more accurate analysis of the solution (15) seems to be impossible without the information concerning the form of the function $w = w(\varrho, P)$; however, Eq. (13) suggests that once the function are known, we can attempt to investigate the higher approximations corresponding to the shell model of surface tension, i.e. such a model of the surface of separation in which σ is assumed to depend on the shape of the surface; we can then analyse the orders of the effects and decide upon the problem of applicability of the shell model.

Appendix

Equation (5) may be written in the form

$$\text{(A1)}\qquad -\frac{\partial(\varrho w)}{\partial\varrho}+2\frac{\partial^2(\varrho w)}{\partial I\partial\varrho}\varrho_{,i}\varrho_{,k}g^{ik}+4\frac{\partial^2(\varrho w)}{\partial I^2}\varrho_{,ij}\varrho_{,k}\varrho_{,m}g^{ik}g^{jm}+2\frac{\partial(\varrho w)}{\partial I}\varrho_{,ij}g^{ij}.$$

In the coordinate system assumed here $\varrho_{,3}\neq 0$, $\varrho_{,1}=\varrho_{,2}=0$, while $g^{33}=1$, and hence

$$\text{(A2)}\qquad \varrho_{,i}\varrho_{,k}g^{ik}=\varrho_{,3}\varrho_{,3}g^{33}=\varrho'^2.$$

By introducing the coordinates u_α $(\alpha=1,2)$ on the surface P, the position vector may be written as

$$\text{(A3)}\qquad \mathbf{R}(u_\alpha,s)=\mathbf{R}_0(u_\alpha)-s\mathbf{n}_0(u_\alpha),$$

the symbol 0 referring to the values taken at the surface P. The base vectors are

$$\text{(A4)}\qquad \mathbf{e}_\alpha=\mathbf{e}_{0\alpha}+s\frac{\partial\mathbf{n}_0}{\partial u_\alpha}=\mathbf{e}_{0\alpha}+sb_{0\alpha\beta}\mathbf{e}_0^\beta,\qquad \mathbf{e}_3=-\mathbf{n}_0,$$

whence

$$\text{(A5)}\qquad \begin{gathered} g_{\alpha\beta}=g_{0\alpha\beta}+2sb_{0\alpha\beta}+s^2b_{0\alpha\gamma}b_{0\beta}^\gamma,\\ g_{33}=1,\quad g_{3\alpha}=0,\quad g^{3\alpha}=0,\quad g^{33}=1.\end{gathered}$$

The Christoffel symbols are given by

$$\text{(A6)}\qquad \begin{Bmatrix}3\\ \alpha\beta\end{Bmatrix}=-\frac{\partial\mathbf{e}_\alpha}{\partial u^\beta}\mathbf{n},\quad \begin{Bmatrix}3\\ 3\alpha\end{Bmatrix}=0,\quad \begin{Bmatrix}3\\ 33\end{Bmatrix}=0.$$

The assumption of parallelism of the equal density surfaces yields $\varrho_{,\alpha}=0$, and hence

$$\text{(A7)}\qquad \varrho_{,ij}\varrho_{,k}\varrho_{,m}g^{ik}g^{jm}=\varrho_{,33}\varrho_{,3}\varrho_{,3}=\left(\frac{\partial^2\varrho}{\partial s^2}-\begin{Bmatrix}3\\ 33\end{Bmatrix}\varrho_{,3}-\begin{Bmatrix}\alpha\\ 33\end{Bmatrix}\varrho_{,\alpha}\right)\left(\frac{\partial\varrho}{\partial s}\right)^2=\varrho''\varrho'^2,$$

$$\text{(A8)}\qquad \varrho_{,jk}g^{jk}=\left(\frac{\partial^2\varrho}{\partial x^j\partial x^k}-\begin{Bmatrix}l\\ jk\end{Bmatrix}\frac{\partial\varrho}{\partial x^l}\right)g^{jk}\qquad (l,k=1,2,3).$$

From the same assumption it follows that

$$\text{(A9)}\qquad \frac{\partial^2\varrho}{\partial s\partial u^\alpha}=0,\qquad \frac{\partial^2\varrho}{\partial u^\alpha\partial u^\beta}=0$$

and

$$\text{(A10)}\qquad \varrho_{,jk}g^{jk}=\frac{\partial^2\varrho}{\partial s^2}-\begin{Bmatrix}3\\ ik\end{Bmatrix}\frac{\partial\varrho}{\partial s}g^{ik}=\frac{\partial^2\varrho}{\partial s^2}-\begin{Bmatrix}3\\ \alpha\beta\end{Bmatrix}g^{\alpha\beta}.$$

Applying the relation (A6) we obtain

$$\text{(A11)}\qquad -\begin{Bmatrix}3\\ \alpha\beta\end{Bmatrix} = -\frac{\partial \mathbf{e}_\alpha}{\partial u^\beta}\cdot \mathbf{n} = \frac{\partial \mathbf{n}}{\partial u^\beta}\cdot \mathbf{e}_\alpha = -b_{0\beta\gamma}\mathbf{e}_0^\gamma\cdot \mathbf{e}_\alpha,$$

$$\mathbf{e}_0^\gamma\cdot \mathbf{e}_\alpha = \mathbf{e}_0^\gamma\cdot(\mathbf{e}_{0\alpha}+sb_{0\alpha\delta}\mathbf{e}_0^\delta).$$

We can always assume $\mathring{g}_{\alpha\beta} = \delta_{\alpha\beta}$, and then

$$\text{(A12)}\qquad \mathring{\mathbf{e}}_0^\gamma\cdot \mathbf{e}_\alpha = \delta_\alpha^\gamma + sb_{0\alpha}^\gamma$$

and

$$\text{(A13)}\qquad \frac{\partial \mathbf{e}_\alpha}{\partial u^\beta}\cdot \mathbf{n} = -b_{0\alpha\beta} - sb_{0\beta\gamma}b_{0\alpha}^\gamma.$$

Let us now select the coordinates u_α so as to render the matrix $b_{\alpha\beta}$ diagonal. Then

$$\text{(A14)}\qquad \det|g_{\alpha\beta}| = \begin{vmatrix}1+2sb_{11}+s^2b_{11}^2 & 0\\ 0 & 1+2sb_{22}+s^2b_{22}^2\end{vmatrix},$$

and thus

$$\text{(A15)}\qquad g^{11} = \frac{1}{(1+sb_{11})^2},\quad g^{22} = \frac{1}{(1+sb_{22})^2},\quad g^{12} = 0.$$

From Eq. (A11) we also obtain

$$\text{(A16)}\qquad \begin{Bmatrix}3\\ 1\ 2\end{Bmatrix} = 0,\quad \begin{Bmatrix}3\\ 2\ 1\end{Bmatrix} = 0$$

and, finally,

$$\text{(A17)}\qquad \begin{Bmatrix}3\\ \alpha\beta\end{Bmatrix} g^{\alpha\beta} = \frac{b_{011}+2sb_{011}b_{022}+b_{022}}{1+s(b_{011}+b_{022})+s^2b_{011}b_{022}} = \frac{2H+2Ks}{1+2Hs+Ks^2},$$

what leads to the result

$$\text{(A18)}\qquad \varrho_{,jk}g^{jk} = \varrho'' + \frac{2H+2Ks}{1+2Hs+Ks^2}\varrho'.$$

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