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Properties of the Gibbs Potential and the Equilibrium of a Liquid with Its Vapor (*).

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SOMMARIO - A partire da alcune proprietà qualitative del potenziale di Gibbs e quindi della funzione di stato di un fluido non viscoso, si prova che è possibile soddisfare le condizioni di equilibrio del sistema di un liquido e del suo vapore separati da un'interfaccia piana o sferica purchè i volumi specifici del liquido e del suo vapore ed il raggio dell'interfaccia sferica varino in intervalli opportuni.

SUMMARY - Starting from some qualitative properties of the Gibbs potential and consequently of the state function of a nonviscous fluid, it is proved that the equilibrium conditions of the system of a liquid and its vapor, which are separated by a plane or spherical interface, can be satisfied provided that the specific volumes of the liquid and its vapor as well as the radius of the spherical interface belong to suitable intervals.

1. Introduction.

In a paper of mine [1] I obtained the set of equations, boundary data and jump conditions for the thermodynamical equilibrium of a system which consists of a liquid and its vapor separated by an interface S. Among the other things in [1] I proved that the solution of the one-dimensional equilibrium problem corresponding to a plane

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interface is carried out by two consecutive steps. First of all the mass density values ϱ^-, ϱ^+ on the two sides of $\mathcal{S}$ can be determined by a system of two scalar equations which represent the jump across $\mathcal{S}$ of the pressure and the Gibbs potential. Afterwards the values ϱ^-, ϱ^+ are taken as initial data of the first order differential equation whose unknown is the mass density of the two phases. The solutions corresponding to these Cauchy problems supply the mass densities of the liquid and its vapor and consequently the external pressure value which is needed in order to have the equilibrium of the two phases. However, in paper [1] no criterion is given to assure the solvability of the jump system.

In this paper I begin with observing that, also in the case of spherical interface, the equilibrium problem splits again in the two aforesaid partial problems. Moreover, by supposing that the Gibbs potential satisfies suitable conditions, I prove that the jump system concerning a plane or a spherical interface $\mathcal{S}$ has one and only one solution ϱ^-, ϱ^+ provided that ϱ^-, ϱ^+ and the radius of $\mathcal{S}$ belong to convenient intervals depending on the temperature. These results can be also geometrically formulated and they supply a practical criterion to obtain ϱ^-, ϱ^+. Such a criterion, which is applicable to a plane or spherical interface, is different in form but equivalent to a generalization of the Maxwell rule when the interface is plane (see [2], [3]). Moreover, these results include the ones that Serrin proved in [4] starting from the Korteweg theory [5], in which the interface is sobstituted by a narrow layer across which the mass density, pressure, etc. change fast but continuously.

2. The equilibrium system for plane or spherical interfaces.

The complete set of equations, boundary data and jump conditions which have to be satisfied in order to obtain the termodynamical equilibrium of a system with a spherical interface $\mathcal{S}$, is obtained from system (4.1) of [1] by inserting into it the mean curvature H of $\mathcal{S}$ equal to $1/R$, R being the radius of $\mathcal{S}$. If we suppose, only for the sake of semplicity, that there are no external body forces, we have

$$(2.1) \qquad \operatorname{grad} p = 0 \qquad \text{in } \mathring{\mathcal{C}}_1 \cup \mathring{\mathcal{C}}_2$$

$$\gamma_\alpha = 0 \qquad \text{on } \mathcal{S}$$

(2.2) $$\frac{2\gamma}{R} = \text{const} \equiv c > 0 \qquad \text{on } \mathcal{S}$$

(2.3) $$[\![p]\!] = c \qquad \text{on } \mathcal{S}$$

$$[\![g(p)]\!] = 0 \qquad \text{on } \mathcal{S}$$

(2.4) $$p = p_e \qquad \text{on } \partial\mathcal{C}' \subset \partial\mathcal{C}$$

$$\partial\mathcal{C}'' = \partial\mathcal{C} - \partial\mathcal{C}'$$

is assigned together with the raccordement angle on $\partial\mathcal{S} \cap \partial\mathcal{C}$.

Here $\mathcal{C}_1$ and $\mathcal{C}_2$ are the regions respectively occupied by the liquid and its vapour, $\mathcal{C} = \mathcal{C}_1 \cup \mathcal{C}_2$, p is the pressure, $\gamma > 0$ is the surface tension (1) and $g(p)$ the Gibbs specific potential.

Owing to the absence of the external body forces (2), system (2.1)-(2.4) can be analysed in the following way. Let us suppose the existence of a suitable value c_M such that for every $c \in (0, c_M]$, system (2.3) admits one and only one solution p^-, p^+. For equation $(2.1)_1$, these values p^-, p^+ coincide with the determinations of p in $\mathcal{C}_1$ and $\mathcal{C}_2$ respectively

(2.5) $$p_1(\varrho_1) = p_1(\varrho^-) = p^-, \qquad p_2(\varrho_2) = p_2(\varrho^+) = p^+$$

so that it is useless to distinguish between p_1 and p^- (p_2 and p^+). We can evaluate the external pressure p_e on the boundary $\partial\mathcal{C}'$. In fact, if $\partial\mathcal{C}' \subset \partial\mathcal{C}_2$, we have $p_e = p_2$. When the functions $p_1(\varrho), p_2(\varrho)$ are invertible, we can derive the values $\varrho^-, \varrho^+, \varrho_1, \varrho_2$.

In the next section we give conditions on the Gibbs potential to assure the existence of one and only one solution p^-, p^+ of system (2.3).

(1) Here we assume that γ does not depend on R. This hypothesis is in accordance with the experience in a wide range of values of R [6].

(2) In the presence of external forces whose specific density is $\boldsymbol{b}$, equation $(2.1)_1$ behaves $\operatorname{grad} p = -\varrho \boldsymbol{b}$, where ϱ is the mass density. Recalling the state equation $p = p(\varrho)$, it results that the unknowns of the system (2.1) are the mass densities ϱ_1 and ϱ_2 of the liquid and vapor respectively.

3. Hypotheses on the state equation.

According to the experimental results, we suppose that the pressure p, regarded as a function of the specific volume $v = 1/\varrho$ and the absolute temperature $\theta > 0$, is defined on a subset D of $(b, \infty) \times (\theta_*, \infty)$ where b and θ_* are suitable values of the specific volume and temperature depending on the material which is described by $p(v, \theta)$. We assume the following properties for D and $p(v, \theta)$:

i) a critical value θ_c of θ exists such that for every $\theta > \theta_c$, the function $p(\cdot, \theta) \in C^1(b, \infty)$ and in (b, ∞) it results $\partial p/\partial v < 0$; moreover,

$$\lim_{v \to b} p(v, \theta) = \infty, \qquad \lim_{v \to \infty} p(v, \theta) = 0 . \tag{3.1}$$

ii) for every $\theta \in (\theta_*, \theta_c)$, the function $p(\cdot, \theta) \in C^1[(b, v_1(\theta)) \cup \cup (v_2(\theta), \infty)]$ where $v_1(\theta) < v_2(\theta)$ and

$$\lim_{\theta \to \theta_c} v_1(\theta) = \lim_{\theta \to \theta_c} v_2(\theta) ;$$

moreover, in $(b, v_1(\theta)) \cup (v_2(\theta), \infty)$ it is $\partial p/\partial v < 0$. Conditions (3.1) are valid too and we have

$$p_1 = p(v_1, \theta) < p_2 = p(v_2, \theta) , \qquad \lim_{v \to v_1} \frac{\partial p}{\partial v} = \lim_{v \to v_2} \frac{\partial p}{\partial v} = 0 . \tag{3.2}$$

Properties i), ii) are satisfied by the experimental isothermal curves of Andrews; their behavior is represented in fig. 2.

In order to semplify the notations, from now on, we eliminate the temperature θ in the next formulas. Keeping this in mind, we observe that for $\theta > \theta_c$ the function $p(v)$ is invertible on (b, ∞) and the inverse function

$$v(p) : (0, \infty) \to (v_1, 0) \tag{3.3}$$

is decreasing; similarly, when $\theta < \theta_c$, by inverting the decreasing function $p(v)$ on (b, v_1) and (v_2, ∞) respectively, we have two functions

$$v_1(p) : (p_1, \infty) \to (b, v_1) , \qquad v_2(p) : (0, p_2) \to (v_2, \infty) . \tag{3.4}$$

Recalling the fundamental thermodynamical relations $v(p) = \partial g/\partial p$, we can obtain two branches of $g(p)$ corresponding to $v_1(p)$ and $v_2(p)$ that are defined but for an arbitrary function Φ_i of θ

$$g_i(p) = \int v_i(p)\, dp + \Phi_i\,, \qquad i = 1, 2\,.$$

Taking into account the trivial relations:

$$\frac{\partial g}{\partial p} = v(p)\,, \quad \frac{\partial^2 g}{\partial p^2} = \frac{\partial v}{\partial p} = \left(\frac{\partial p}{\partial v}\right)^{-1} < 0\,, \quad (p \neq p_1, p_2) \tag{3.5}$$

we can say that the functions $g_1(p)$, $p \in (p_1, \infty)$ and $g_2(p)$, $p \in (0, p_2)$ are always increasing on their intervals of existence and they exhibit the convexity upwards. Moreover, being

$$v_1(p') < v_2(p'')\,, \qquad \forall p' \in (p_1, \infty),\ p'' \in (0, p_2) \tag{3.6}$$

at every point, the function $g_1(p)$ has a slope less steep than the corresponding one of the curve $g_2(p)$.

It is not possible to determine the positions of these curves on the plane (p, g) because the functions $g_1(p)$ and $g_2(p)$ are not completely assigned owing to the arbitrariness of functions Φ_1 and Φ_2 of the temperature. In order to reduce this indetermination of g_1 and g_2, along with the properties of g_1 and g_2 above derived from i) and ii), we assume that

iii) for every $\theta < \theta_c$ a value $p_0 \in (p_1, p_2)$ exists such that

$$g_1(p_0) = g_2(p_0) \tag{3.7}$$

(see fig. 1) and moreover

$$\lim_{p\to\infty} g_1(p) = \infty\,, \qquad \lim_{p\to 0} g_2(p) = -\infty\,.$$

It is obvious that condition (3.7) is equivalent to the existence of a solution for system (2.2), (2.3) with a plane interface. It is also convenient to observe that (3.7) determines the difference $\Phi_1 - \Phi_2$; therefore, for $\theta \in (\theta_*, \theta_c)$, $g_1(p)$ and $g_2(p)$ are determined but for the same arbitrary parallel translation to the g-axis. As it will be proved in the next section, the remaining arbitrariness of g_1 and g_2 does not affect the physical results. Finally we observe that (3.7) and the previous considerations imply

$$g_2(p) < g_1(p)\,, \qquad p \in (p_1, p_0) \tag{3.8}$$

$$g_2(p) > g_1(p)\,, \qquad p \in (p_0, p_2)\,. \tag{3.9}$$

4. Solutions of the jump system for spherical interface.

In order to prove an existence and uniqueness theorem for system (2.2), (2.3), we start with the positions

$$\mathfrak{g}_1 = g_1(p_1)\,, \qquad \mathfrak{g}_0 = g_1(p_0) = g_2(p_0)\,, \qquad \mathfrak{g}_2 = g_2(p_2)\,, \tag{4.1}$$

and the proof of the *following*.

TH. 1. *The functions g_1 and g_2 are both invertible on the interval* $[\mathfrak{g}_1, \mathfrak{g}_0]$; *moreover, on* $[\mathfrak{g}_1, \mathfrak{g}_0]$ *the difference*

$$g_2^{-1}(\mathfrak{g}) - g_1^{-1}(\mathfrak{g})$$

is positive, decreasing and it vanishes at $\mathfrak{g}_0$.

PROOF. Function $g_1(p)$ increases in $[p_1, \infty)$ and so it is invertible on $[p_1, p_0] \subset [p_1, \infty)$. Similarly, function $g_2(p)$ increases on $(0, p_2]$. Being $p_1 < p_0 < p_2$, it is invertible on $[p_1, p_0]$ too. By (3.8) and (3.7) we have $g_2([p_1, p_0]) = [g_2(p_2), \mathfrak{g}_0] \subset [\mathfrak{g}_1, \mathfrak{g}_0]$. Therefore, on the interval $[\mathfrak{g}_1, \mathfrak{g}_0]$ both the functions $g_1^{-1}(\mathfrak{g})$ and $g_2^{-1}(\mathfrak{g})$ exist and they are increasing because $(d/d\mathfrak{g})g_i^{-1}(\mathfrak{g}) = 1/v_i(p) > 0$. Finally, from

$$\frac{d}{d\mathfrak{g}}\left(g_2^{-1}(\mathfrak{g}) - g_1^{-1}(\mathfrak{g})\right) = \frac{v_1(p) - v_2(p)}{v_1(p)v_2(p)} < 0$$

(see (3.8)), we conclude that the difference $g_2^{-1}(\mathfrak{g}) - g_1^{-1}(\mathfrak{g})$ is positive, decreasing in $[\mathfrak{g}_1, \mathfrak{g}_0]$ and vanishing at $\mathfrak{g}_0$.

If we introduce the notation $g_2^{-1}(\mathfrak{g}_1) = p_v^*$ and we recall that $g_1^{-1}(\mathfrak{g}_1) = p_1$, the previous result allows us to say that the difference $g_2^{-1}(\mathfrak{g}) - g_1^{-1}(\mathfrak{g})$ attains its maximum $p_v^* - p_1$ at $\mathfrak{g}_1$, decreases in the interval $[\mathfrak{g}_1, \mathfrak{g}_0]$ and vanishes at g_0. By setting

$$R_m = \frac{2\gamma}{p_v^* - p_1}, \tag{4.3}$$

we are now in the condition to prove the following:

TH. 2. *If the temperature θ is fixed in the interval (θ_*, θ_c) for each value of $c \in (0, p_v^* - p_1]$, system (2.2), (2.3) has one and only one solution (p_l, p_v, R) where $p_l \in [p_1, p_0), p_v \in [p_v^*, p_0)$ and $R \in (R_m, \infty)$.*

PROOF. Owing to the previous theorem, the equation

$$g_2^{-1}(\bar{\mathfrak{g}}) - g_1^{-1}(\bar{\mathfrak{g}}) = c \tag{4.4}$$

has one and only one solution $\bar{\mathfrak{q}}$ if and only if $c \in (0, p_v^* - p_1]$. On the other hand, being g_2^{-1} and g_1^{-1} invertible on $[\mathfrak{g}_1, \mathfrak{g}_0]$, to every solution $\bar{\mathfrak{g}}$ of (4.4) one and only one couple (p_l, p_v) there corresponds such that

$$g_1^{-1}(\bar{\mathfrak{g}}) = p_l, \quad g_2^{-1}(\bar{\mathfrak{g}}) = p_v \tag{4.5}$$

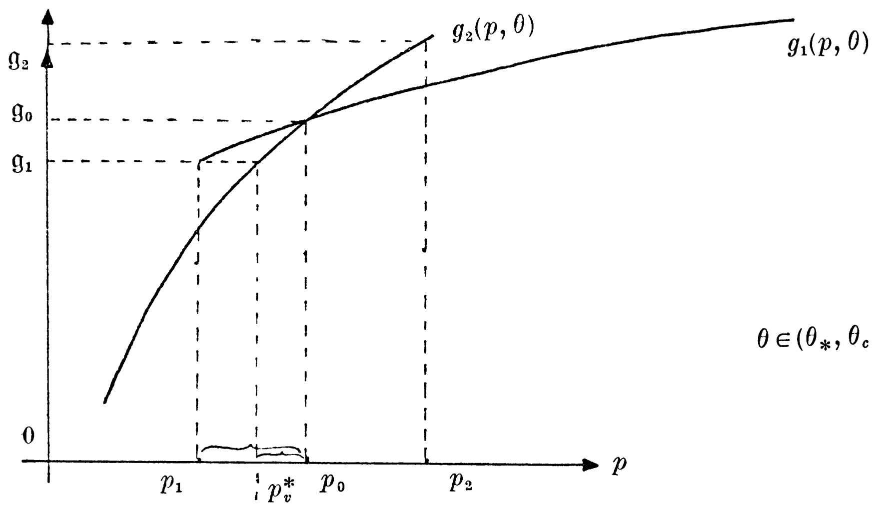
where $p_v \in [p_v^*, p_0)$, $p_l \in [p_1, p_0)$. But these values of the pressure satisfy jump system (2.4). In fact, (4.5) is equivalent to the equation

$$\bar{\mathfrak{g}} = g_1(p_l) = g_2(p_v)$$

and moreover (4.4) and (4.5) imply $p_v - p_l = c > 0$. Finally to every $c \in (0, p_v^* - p_l]$ can be associated a radius R for the spherical interface given by $R = 2\gamma/c$ which belongs to the interval $[R_m, \infty)$ since $c = p_v^* - p_1$ is the greatest value of c (see figs. 1 and 2).

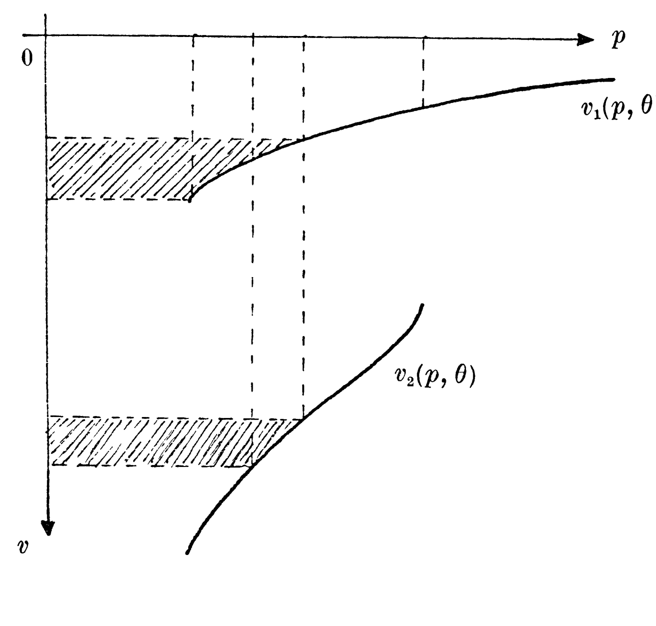
It is clear that in a specific problem we have to take into account the particular boundary conditions (2.4). Therefore, we can accept only those solutions of system (2.2), (2.3) which satisfy the boundary conditions. In particular, if we suppose that the vapor is internal to spheres all contained in the liquid (bubbles), so that $\partial\mathcal{S} \cap \partial\mathcal{C} = \emptyset$, from theorem 2 we derive:

TH. 3. *If the temperature θ is fixed in the interval (θ_*, θ_c), a liquid at uniform pressure $p_l \in [p_1, p_0)$ is at equilibrium with its vapor if and only if the vapor is at a suitable pressure $p_v \in [p_v^*, p_0)$ and it is contained into bubbles of a fixed radius $R \in [R_m, \infty)$.*



$g_2(p, \theta)$
$g_1(p, \theta)$
g_2
g_0
g_1
$\theta \in (\theta_*, \theta_c)$
0
p
p_1
p_v^*
p_0
p_2

Fig. 1.



0
p
$v_1(p, \theta)$
$v_2(p, \theta)$
v

Fig. 2.

It is worthwhile to observe that, when the functions $p_1(v)$, $p_2(v)$, $g_1(p)$, $g_2(p)$ are assigned (these last two being defined except for a constant), it is possible to evaluate the values of p_v, R, v_l, v_v for every $p_l \in [p_1, p_0)$.

Similarly, if we put $p_l^* = g_2^{-1}(g_2)$, it is possible to prove the following

TH. 4. *If the temperature θ is fixed in the interval (θ_*, θ_c), a vapor at a uniform pressure $p_v \in (p_0, p_2]$ is at equilibrium with drops of radius R of its liquid if and only if the liquid has a suitable pressure $p_l \in (p_0, p_l^*]$ and $R \in [2\gamma/(p_l^* - p_2), \infty]$.*

Theorems 3 and 4 lead to the same results that Serrin proved in [4] starting from the Kortweg theory of capillarity.

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