THE FORM OF INTERFACIAL SURFACES IN KORTEWEG'S THEORY OF PHASE EQUILIBRIA*

By

JAMES SERRIN

University of Minnesota

1. Introduction. In order to provide a continuum mechanical model for capillarity, the Dutch physicist D. J. Korteweg many years ago proposed a form for the (Cauchy) stress tensor which includes terms depending on density variations in the fluid [6]. This theory of Korteweg, although dormant for nearly 75 years, has recently become the object of renewed interest since it turns out to give an approach to the problem of liquid-vapor phase transitions in fluids which is purely mechanical in basis, and which can be used to supplement standard thermostatic equilibrium theory in important ways [1, 2, 4, 5].

Pursuant to this revival of interest, we shall here show that, *unless rather special conditions are satisfied*, the only geometric phase boundaries which are consistent with Korteweg's theory are either spherical, cylindrical, or planar. That is (the effect of gravity always being ignored), the physical situations which can occur in phase transitions governed by Korteweg's theory are either spherical liquid bubbles in an ambient vapor atmosphere, spherical vapor bubbles in an ambient liquid bath, planar interfaces between the phases, or finally (no doubt unstable) circular cylindrical interfaces between the phases. This rather surprising conclusion can perhaps be best understood as a consequence of the fact that the mechanical equations of equilibria (Cauchy's equations) have three independent components while liquid-vapor phase equilibria are determined by just one physical variable—the density.

From a physical point of view our result mirrors the tendency of surface tension to produce phase boundaries which have constant mean curvature; in the present circumstances, however, this tendency is seen in an extreme isoperimetric form.

Since we will be dealing with an overdetermined system of partial differential equations the result can also be viewed from a purely mathematical point of view. In fact, when reduced to its essentials, the problem becomes precisely that of determining the local structure of solutions of the system

$$\Delta u = h(u), \qquad |\operatorname{grad} u| = g(u),$$

where u is a twice continuously differentiable real function defined on some open connected set in $\mathbb{R}^3$ and $h(u) \in C^0$, $g(u) \in C^1$ are functions defined on the range of u,

* Received November 29, 1982.

with $g(u) \neq 0$. In this situation, Pucci [3] has shown that *any solution of this system necessarily has level surfaces which are either (pieces of) concentric spheres, or concentric circular cylinders, or parallel planes.* Applying this result to Korteweg's theory then leads to the principal conclusions of the paper.

In the following section we derive the differential equations of Korteweg's equilibrium theory, and in Sec. 3 we apply Pucci's result to determine the local behavior of solutions. Finally, in Sec. 4, we treat the global behavior of phase interfaces, the main results being contained in Theorems 2 and 3. We conclude with several remarks which relate our results to earlier studies of the Korteweg equations and finally discuss whether the *special conditions* noted above should in fact be required whenever the theory is used.

2. Korteweg's equilibrium theory. Equilibrium configurations of continuous media are governed by the well-known Cauchy equations

$$\frac{\partial \tau_{ij}}{\partial x_j} = 0, \qquad i = 1, 2, 3, \tag{1}$$

where τ_{ij} is the Cauchy stress tensor, and the natural summation convention is applied for repeated indices. For fluids in which long-range molecular interactions are significant to equilibrium, as in the case of phase transitions, Korteweg [6] proposed the following form for the stress tensor:

$$\tau_{ij} = -pI_{ij} + v_{ij} \tag{2}$$

where I_{ij} is the Kronecker symbol and

$$v_{ij} = \left(\alpha \Delta\rho + \beta \,|\, \nabla\rho \,|^2\right) I_{ij} + \left(\gamma \frac{\partial^2 \rho}{\partial x_i \partial x_j} + \delta \frac{\partial \rho}{\partial x_i} \frac{\partial \rho}{\partial x_j}\right).$$

Here $p = p(\rho)$ is a given function representing the pressure of the fluid in terms of its density ρ; the coefficients α, β, γ, δ are again functions of density, representing long-range molecular effects; $\Delta\rho$ is the Laplacian of ρ; and we have written (as we shall occasionally also write in the sequel) $\nabla\rho$ for grad ρ. Ordinarily the functions p, α, β, γ, δ depend on the fluid temperature as well as on the density. Since we are dealing with fluid equilibrium, however, one can suppose that the temperature is a given constant, equal to the ambient temperature of the surroundings; accordingly it can be suppressed in the formulation of the problem.

If the expression (2) is used to eliminate τ_{ij} from (1) we are left with three partial differential equations for the single physical parameter ρ, considered as a function of the space variables x_1, x_2, x_3. These equations have been discussed in the plane case in [1, 2, 5], and in the radially symmetric case in unpublished work of the author.

For general three dimensional configurations there have been no previous studies. Here we shall show that, *unless the Korteweg coefficients satisfy certain quite special conditions*, the only possible equilibrium configurations are those in which the density function $\rho(x_1, x_2, x_3)$ has level surfaces which are pieces of

(a) concentric spheres, or

(b) concentric circular cylinders, or

(c) parallel planes.

Physically speaking, a region in which there is a rapid transition of density from one value to another represents an interfacial layer between fluid phases. Consequently we can interpret our result to show, as stated in the introduction, that the only geometric phase boundaries which are consistent with Korteweg's theory are either spherical, cylindrical, or planar (unless certain special conditions are met).

In order to carry out this program, we first eliminate τ_{ij} between (1) and (2) to obtain

$$\frac{\partial}{\partial x_i}\left(-p + a\Delta\rho + b\,|\nabla\rho|^2\right) + c\left(\frac{\partial^2\rho}{\partial x_i \partial x_j}\frac{\partial\rho}{\partial x_j} - \Delta\rho\frac{\partial\rho}{\partial x_i}\right) = 0,$$

where

$$a = \alpha + \gamma, \quad b = \beta + \delta, \quad c = \gamma' - \delta$$

and primes denote differentiation with respect to ρ. Without difficulty, the above equation can be rewritten in the vector form

$$\operatorname{grad}\left(-p + a\Delta\rho + \left(b + \frac{1}{2}c\right)|\nabla\rho|^2\right) = \left(c\Delta\rho + \frac{1}{2}c'\,|\nabla\rho|^2\right)\operatorname{grad}\rho. \tag{3}$$

It is this equation which we shall use in what follows.

Naturally, precise conditions on the coefficients a, b, c must be given, together with a formal statement of the specific differentiability class of a solution function $\rho(x_1, x_2, x_3)$. In particular we shall suppose concerning the coefficients that

(i) a, b are continuous functions of the density, and

(ii) c is continuously differentiable.

By a solution of (3) in a domain Ω we shall mean a twice continuously differentiable function ρ such that

$$-p + a\Delta\rho + \left(b + \tfrac{1}{2}c\right)|\nabla\rho|^2 \in C^1 \tag{4}$$

and for which (3) is satisfied everywhere in Ω. Note that condition (4) may hold even when the density is *not* three times differentiable.

3. Local behavior. This section consists of a purely mathematical study of the principal equation (3) of Korteweg's theory. We begin with a well-known result of analysis, proved here however under relatively minimal hypotheses.

LEMMA 1. Let F, G, and u be real functions defined on some open region Ω in $\mathbb{R}^3$, such that (in Ω)

(i) F and u are continuously differentiable

(ii) $\operatorname{grad} F = G \operatorname{grad} u$.

If $\operatorname{grad} u \neq 0$ at a point $P \in \Omega$, then there exists a neighborhood Ω' of P and a continuously differentiable function $f\colon \mathbb{R} \to \mathbb{R}$ such that

$$F = f \circ u, \qquad G = f' \circ u \quad \text{in } \Omega'.$$

Proof. By appropriately rotating coordinates at P we can assume (in a rectangular system x, y, z)

$$\frac{\partial u}{\partial z} \neq 0 \quad \text{at } P.$$

Consequently by the implicit function theorem there exists a neighborhood $\tilde{\Omega}$ of P in which x, y, u are allowable coordinates, diffeomorphically related to x, y, z. Write

$$\Phi(x, y, u) = F(x, y, z(x, y, u)), \qquad \Psi(x, y, u) = G(x, y, z(x, y, u))$$

so that Φ is of class C^1 in $\tilde{\Omega}$. Clearly

$$\text{grad } F = \frac{\partial \Phi}{\partial x}\vec{i} + \frac{\partial \Phi}{\partial y}\vec{j} + \frac{\partial \Phi}{\partial u} \text{ grad } u$$

so from the condition grad $F = G$ grad u (since grad u is linearly independent of $\vec{i}, \vec{j}$ in $\tilde{\Omega}$).

$$\frac{\partial \Phi}{\partial x} = \frac{\partial \Phi}{\partial y} = 0, \qquad \frac{\partial \Phi}{\partial u} = \Psi.$$

Thus $\Phi = f(u)$ in some (possible smaller) neighborhood Ω' of P. In turn $\Psi = df/du$ in Ω', which is the required conclusion.

LEMMA 2. Suppose that the coefficients p, a, b, c in equation (3) satisfy the conditions (i), (ii), and also

$$A \equiv bc + \tfrac{1}{2}(c^2 - ac') \neq 0.$$

Let ρ be a solution of (3) in some open set Σ of $\mathbb{R}^3$, with grad $\rho \neq 0$ in Σ. Then in the neighborhood of any point P of Σ equation (3) can be reduced to the form

$$|\nabla\rho| = g(\rho), \qquad \Delta\rho = h(\rho),$$

where g is a continuously differentiable function and h a continuous function of ρ.

Proof. Taking $u = \rho$ and

$$\begin{cases} F = -p + a\Delta\rho + \left(b + \tfrac{1}{2}c\right)|\nabla\rho|^2, \\ G = c\Delta\rho + \tfrac{1}{2}c'|\nabla\rho|^2 \end{cases} \tag{5}$$

in Lemma 1, and using equation (3), we see that for each point $P \in \Sigma$ there exists a corresponding neighborhood Σ' of P and a C^1 function $f\colon \mathbb{R} \to \mathbb{R}$ such that

$$F = f \circ \rho, \qquad G = f' \circ \rho \quad \text{in } \Sigma'.$$

In turn, from (5) we get easily

$$\Delta\rho = (1/A)\left\{\left(b + \tfrac{1}{2}c\right)f' - c'(f + p)\right\} \equiv h(\rho),$$
$$|\nabla\rho|^2 = (1/A)\{c(f + p) - af'\} \equiv \{g(\rho)\}^2$$

in Σ'. Now $|\nabla\rho|^2$ is continuously differentiable since ρ is of class C^2. This implies (since x, y, ρ are coordinates in Σ') that $g\colon \mathbb{R} \to \mathbb{R}$ is equally of class C^1. It is obvious that $h(\rho)$ is continuous.

Naturally $g(\rho) \neq 0$ since grad $\rho \neq 0$.

It follows now from Pucci's theorem [3] that the level surfaces of ρ in some neighborhood of P must be either concentric spheres, concentric circular cylinders or parallel planes. By an elementary chaining argument this conclusion obviously extends to the entire set Σ where grad $\rho \neq 0$. We state this formally as

THEOREM 1. Suppose that the coefficients p, a, b, c in equation (3) satisfy conditions (i), (ii), and also

$$A \equiv bc + \tfrac{1}{2}(c^2 - ac') \neq 0.$$

Let ρ be a solution of (3) in some connected open set Σ in $\mathbb{R}^3$, with grad $\rho \neq 0$. Then the level sets of ρ are either pieces of concentric spheres, or concentric circular cylinders, or parallel planes (but not combinations of these).

4. Main results. We next turn our attention to the global case, that is when ρ is a solution of (3) in all $\mathbb{R}^3$. Of course in this situation we cannot suppose that grad $\rho \neq 0$ everywhere, a fact which causes some complications. The principal conclusion is the following

THEOREM 2. Suppose that the coefficients p, a, b, c, in equation (3) are continuously differentiable, and also

$$a \neq 0, \qquad A \neq 0.$$

Let ρ be a solution of (3) in $\mathbb{R}^3$, not identically constant. Then the level surfaces of ρ are either concentric spheres, or concentric circular cylinders, or parallel planes (but not combinations of these).

Proof. Since ρ is not identically constant there exists a nonempty connected open set Σ where grad $\rho \neq 0$. By Theorem 1 the level sets of ρ in Σ are either pieces of concentric spheres, concentric circular cylinders, or parallel planes.

What must be shown is that this conclusion holds not only in Σ but in fact in all of $\mathbb{R}^3$. It will be enough to consider the case when the level surfaces in Σ are concentric spheres, since the other two possibilities can be treated using essentially the same arguments. Thus suppose that we have a connected open set Σ, which without loss of generality we can suppose to be a ball, within which grad $\rho \neq 0$ and the level sets of ρ are pieces of concentric spheres, as shown in Fig. 1.

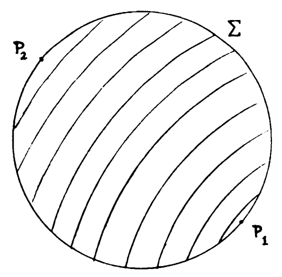

FIG. 1.

Let 0 be the center of the concentric spheres of Σ, and let r denote the spherical coordinate in $\mathbb{R}^3$ with respect to 0 as origin. Obviously $\rho = \rho(r)$ in Σ, with

$$\rho_r = \frac{d\rho}{dr} \neq 0$$

since grad $\rho \neq 0$. This being the case, it follows at once that $\rho_r \neq 0$ at each boundary point of Σ, except possibly the two points P_1 and P_2 where the boundary of Σ is tangent to the concentric spheres (as in Fig. 1 we suppose that 0 lies outside Σ, as can always be assumed without loss of generality). We can now apply an obvious continuation argument, based on Theorem 1, to extend the region in which grad $\rho \neq 0$ and the level sets are concentric spheres to a complete annular shell, as shown in Fig. 2. In particular $\rho = \rho(r)$ in this region, which we shall denote by Γ.

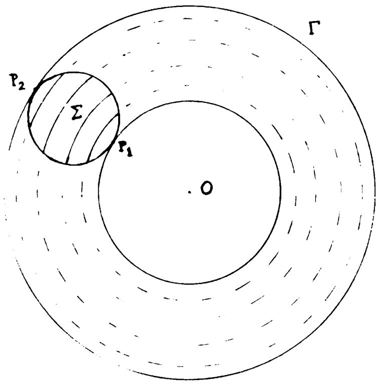

FIG. 2.

Now if grad $\rho \neq 0$ at any boundary point of the shell Γ, then by the radial symmetry it is clear that grad $\rho \neq 0$ at all points of the same boundary component. Another continuation argument based on Theorem 1 then allows one to extend the region Γ in which grad $\rho \neq 0$ and the level sets are concentric spheres to *larger radii* (if the outer boundary of Γ is involved) or to *smaller radii* (if the inner boundary is in question).

Next consider the situation when grad $\rho = 0$ everywhere on the outer spherical boundary of Γ. In other words, we have $\rho = \rho(r)$ in Γ and $\rho =$ constant, $\rho_r = 0$ on the outer boundary.

Suppose for contradiction that also $\rho_{rr} = 0$ on the outer boundary. The differential equation (3) in Γ can be written in polar coordinates in the form

$$\frac{d}{dr}\left\{-p + a\left(\rho_{rr} + \frac{2}{r}\rho_r\right) + b\rho_r^2\right\} = \frac{2c}{r}\rho_r^2, \tag{4}$$

that is

$$\begin{cases} a\sigma_r = -\dfrac{2}{r}a\sigma - b\sigma^2 + \displaystyle\int_{r_0}^{r}\frac{2c}{r}\sigma^2\,dr + p, \\ \rho_r = \sigma. \end{cases} \tag{6}$$

Since $a \neq 0$, and since a, b, c are continuously differentiable, a standard uniqueness theorem for ordinary differential equations[1] now implies that $\rho \equiv$ constant in Γ, this being an obvious solution obeying $\rho_r = \rho_{rr} = 0$ at the outer radius of Γ. But the relation $\rho \equiv$ constant is impossible since grad $\rho \neq 0$ in Γ.

---

[1] Actually (6) is a functional ordinary differential equation, but there is no difficulty adapting the usual proof of uniqueness to it.

Having shown that $\rho_{rr} \neq 0$ on the outer boundary of Γ, it follows that $\rho_{rr} \neq 0$ in some slightly larger spherical shell Γ' surrounding Γ. At the same time $\rho_r = 0$ on the outer boundary of Γ, so obviously $\rho_r \neq 0$ in Γ'. By applying Theorem 1 again we infer that the level surfaces of ρ in Γ' likewise are either pieces of concentric spheres, concentric circular cylinders, or parallel planes. It is evident that this situation is compatible with the behavior of the level surfaces in Γ only if the level surfaces in Γ' are spheres concentric with the spherical level surfaces in Γ.

We can of course apply the same argument at the inner spherical surface of Γ.

From the various cases just considered it follows that the set Γ: $r_0 < r < r_1$ can always be extended to a set Γ^*: $r_0^* < r < r_1^*$ with $r_0^* < r_0$, $r_1^* > r_1$ and with $\rho = \rho(r)$ in Γ^*. Obviously this process never ends unless $r_0^* = 0$, $r_1^* = \infty$, completing the proof of the theorem.

When the solution ρ is not defined in all $\mathbb{R}^3$, but only in some connected open subset of $\mathbb{R}^3$, a straightforward variant of the previous process still applies. Thus we get

THEOREM 3. Suppose that p, a, b, c are continuously differentiable functions of ρ, and that

$$a \neq 0, \qquad A \neq 0.$$

Let ρ be a solution of (3) in some connected open subset Ω of $\mathbb{R}^3$ and suppose ρ is not identically constant. Then the level surfaces of ρ are either pieces of concentric spheres, or pieces of concentric circular cylinders, or pieces of parallel planes (but not combinations of these).

We note in conclusion that the variation of density from one level surface to another is governed in the spherical case by the equation

$$\frac{d}{dr}\left\{-p + a\left(\rho_{rr} + \frac{2}{r}\rho_r\right) + b\rho_r^2\right\} = \frac{2c}{r}\rho_r^2, \tag{7}$$

in the cylindrical case by the equation

$$\frac{d}{dr}\left\{-p + a\left(\rho_{rr} + \frac{1}{r}\rho_r\right) + b\rho_r^2\right\} = \frac{c}{r}\rho_r^2, \tag{8}$$

and in the plane case by the equation

$$\frac{d}{dr}\left\{-p + a\rho_{rr} + b\rho_r^2\right\} = 0. \tag{9}$$

Equation (9) is integrable by quadratures, as shown in [1] and [5], and a fairly complete theory of plane phase transitions is accordingly available. A similar theory for Eqs. (7) and (8) has not yet been developed, since these equations have no simple global theory.

It is interesting that in case $A \equiv 0$ it is possible to obtain first integrals for both (7) and (8), in which case one can in fact develop analogous results to those in [5]. *Thus the condition* $A \equiv 0$ *not only is necessary in order to have nonradially summetric solutions, but equally facilitates the integration of* (7) *and* (8) *in the radial case*!

The question can be raised whether $A \equiv 0$ is a *physically necessary* restriction or the Korteweg coefficients. Without it the theory allows very few equilibrium configurations, as we have demonstrated, a fact which might be considered unusual, but which surely does not force the condition $A \equiv 0$. One may argue that in any any case the Korteweg theory is only an approximation, but this objection can be ascribed to any particular theory: the question really becomes, is the approximation itself a physically realistic one when A is not identically zero? While this question probably cannot be answered in generality without careful analysis of intermolecular forces (cf. eg. [2]), nevertheless it turns out that the second law of thermodynamics—in the form of a generalized Clausius-Duhem inequality—does require $A \equiv 0$, at least if all kinematically allowable motions of the fluid can be realized by the application of some conceivable force system. This hypothesis is itself open to physical criticism, however, both on general principles as well as on the grounds that the required motions, whether or not they can theoretically occur, may in fact be unattainable by virtue of being unstable.

Under the circumstances, one can certainly argue that the present result offers significant further reason to accept the restriction $A \equiv 0$ as necessary for any physically realistic Korteweg fluid.

References

[1] E. C. Aifantis and J. Serrin, *The mechanical theory of fluid interfaces and Maxwell's rule* (to appear)

[2] M. T. Davis and L. E. Scriven, *Stress and structure in fluid interfaces*, Advances in Chemical Physics, 357–454 (1982)

[3] P. Pucci, *An overdetermined system*, *Quarterly of Applied Mathematics*, this issue

[4] M. Slemrod, *Admissibility criteria for propagating phase boundaries in a van der Waals fluid* (to appear)

[5] J. Serrin, *Phase transitions and interfacial layers for van der Waals fluids*, Recent Methods in Nonlinear Analysis and Applications, ed. A. Canfora, et al. Istituto di Matematica, Universitá di Napoli, 1980, 169–175

[6] D. J. Kortweg, *Sur la forme que prennant les équations du mouvement des fluides si l'on tient compte des forces capillaires causées par des vsriations de densité*, Archives Néerlandaises des Sciences Exactes et Naturelles, Series II **6**, 1–24. (1901)