Some results and conjectures in the gradient theory of phase transitions

by

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Abstract.

In the van der Waals - Cahn - Hilliard theory of phase transitions the energy depends not only on the density, but also on the *density gradient*, a dependence introduced to account for the interface between phases. Within this theory the stable density-distributions $u(x)$ for a fluid confined to a container Ω are characterized by the variational problem: (P_h) minimize

$$E_h(u) = \int_\Omega \{W(u(x)) + h^2|\text{grad}u(x)|^2\}dx$$

subject to the constraint

$$\int_\Omega u(x))dx = m.$$

Here $W(u)$ is the coarse-grain energy, assumed nonconvex, h is a constant which characterizes capillary effects, and m is the total fluid mass.

In this paper we discuss recent results and conjectures for Problem P_h; in particular, those relating P_h to the classical problem with $h = 0$. We also discuss a generalization of P_h which includes contact energy between the fluid and the container walls.

1. Classical theory.

Consider a fluid confined to a container which occupies a bounded, open region Ω in $\mathbf{R}^n$. Assume that the energy $W(u)$, per unit volume, is a smooth function of the density u, and that the total mass of fluid in Ω is m, so that the admissible density-distributions satisfy the **constraint**

$$\int_{\Omega} u(x))dx = m. \tag{1.1}$$

Then, if there are no other contributions to the energy, the total energy $E_0(u)$ in any distribution $u(x)$ is given by the functional

$$E_0(u) = \int_{\Omega} W(u(x))dx. \tag{1.2}$$

We seek those density distributions that render the body stable in the sense of Gibbs and hence seek solutions of the variational problem:

(P_0) minimize $E_0(u)$, subject to (1.1), over all u with both u and $W(u)$ in $L^1(\Omega)$.

For this and other variational problems, we will always use the term **solution** to mean *global minimizer*.

We assume that W is *nonconvex*, of a form capable of supporting two phases. Precisely, we assume that W consists of two convex sections separated by a concave segment (cf. Figure 1). We also assume that the two minima u_1 and u_2 have equal energy with

$$W(u_1) = W(u_2) = 0. \tag{1.3}$$

The assumption (1.3) involves no loss of generality; indeed, because of the constraint we can always add an affine function of u to the integrand in (1.2) without changing the solution set of P_0.

Problem P_0 is easily solved. Choose length scale so that[1]

$$\mathrm{vol}(\Omega) = 1,$$

and define

$$V = (u_2 - m)/(u_2 - u_1). \tag{1.4}$$

[1]We write "vol" and "area", respectively, for n- and (n-1)-dimensional Hausdorff measure.

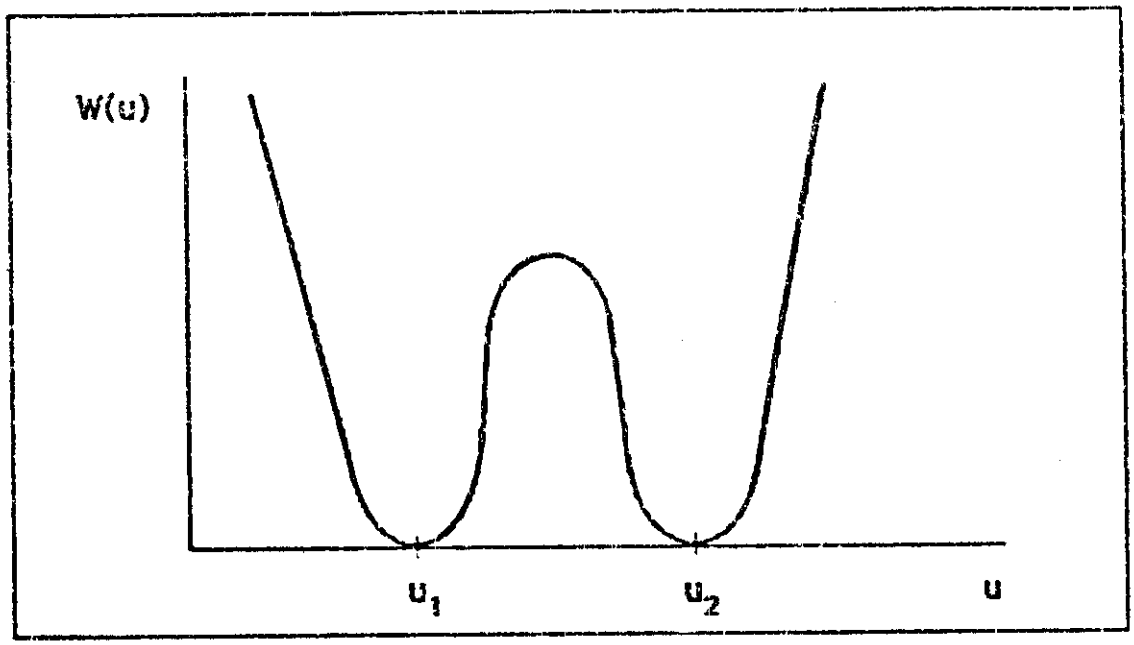

Figure 1. Coarse-grain energy W(u) as a function of density u

Then:
(i) for $m \le u_1$ or $m \ge u_2$ the solution u_0 of P_0 is single phase with $u_0(x) \equiv m$;
(ii) for $u_1 < m < u_2$ all solutions of P_0 are two phase, the solution set consisting of fields of the form

$$\begin{aligned} u_0(x) &= u_1, \quad x \text{ in } F, \\ u_0(x) &= u_2, \quad x \text{ in } \Omega \backslash F, \end{aligned} \tag{1.5}$$

where F is any (measurable) subset of Ω with volume

$$\text{vol}(F) = V. \tag{1.6}$$

A problem with the two-phase solution (ii) is the drastic *lack of uniqueness,* as modulo the volume constraint (1.6) the set F is completely *arbitrary.* This lack of uniqueness arises because *interfaces* (jumps in u) are allowed to form without a concomitant increase in energy.

One might ask: Which of the infinity of solutions (1.5) are *physically preferred?* If the physically-preferred solutions are those that arise as limiting cases within a theory which includes interfacial energy, then one might expect the preferred solutions u_0 to be those which minimize the "area"

$$a(u_0) = \text{area}(\Sigma) \tag{1.7}$$

of the **interface**

$$\Sigma = \partial F \cap \Omega$$

(cf. (1.5) and recall that Ω is open). We are therefore led to the following

Definition. A two-phase solution u_0 of P_0 has **minimal interface** if

$$a(u_0) \le a(u)$$

for any other solution u (corresponding to the same value of m).

The variational problem associated with this definition, namely finding a subset F of Ω that minimizes $\text{area}(\Sigma)$ subject to $\text{vol}(F) = V$, has a large literature.[1] There is existence, but not uniqueness, and solutions are analytic, at least for $n \le 8$. In fact, solutions are surfaces of constant mean-curvature.

[1] Cf., e.g., Massari and Pepe [1]; Giusti [2]; Gonzalez, Massari, and Tamanini [3].

2. The gradient theory.

In a paper [4,5][1] now classic, van der Waals considered fluids whose energy is determined not only by the density, but also by the density gradient.[2] A simple but physically reasonable extension of the classical theory, within van der Waals' framework, is based on the energy[3]

$$E_h(u) = \int_\Omega \{W(u(x)) + h^2|\text{grad}u(x)|^2\}dx. \qquad (2.1)$$

Here $W(u)$, still assumed of the form shown in Figure 1, represents the coarse-grain energy, that is, the energy, per unit volume, when the density is uniform; while $h > 0$ is a small parameter. Note that van der Waals' theory allows for interfacial energy - or more precisely for an increase in energy over regions in which the density undergoes rapid changes.

As before, we seek stable density distributions and hence consider the variational problem:

(P_h) minimize $E_h(u)$ over the set of all u in $H^1(\Omega)$ that satisfy the constraint (1.1).

The **Euler-Lagrange equation** and **natural boundary condition** for this problem are:

$$2h^2\Delta u = W'(u) - \mu \qquad \text{in } \Omega, \qquad (2.2)$$

$$\partial u/\partial n = 0 \qquad \text{on } \partial\Omega, \qquad (2.3)$$

where μ (= constant) is the Lagrange multiplier corresponding to the constraint (1.1). We will refer to μ as the **chemical potential** of u. (This definition is standard for the limiting case $h = 0$.)

Note that for $m \le u_1$ or $m \ge u_2$, Problem P_h has only the single-phase solution $u(x) \equiv m$; for that reason we henceforth restrict our discussion to

$$u_1 < m < u_2.$$

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[1] Cahn and Hilliard [6], apparently unaware of van der Waals' paper, rederived what is essentially van der Waals' theory and, using this theory, obtained several important results concerning the interfacial energy between phases. Since then gradient theories have been used to analyze phase transitions, spinodal decomposition, and other physical phenomena (cf. [5,7] for selected references).

[2] A theory which directly penalizes a sharp interface is given by Gurtin [8].

[3] We use the following notation: grad is the gradient; Δ is the Laplacian; $\partial/\partial n$ is the outward normal derivative on $\partial\Omega$; $W'(u) = dW(u)/du$.

For W sufficiently regular the direct method of the calculus of variations and elementary regularity theory lead to the conclusion that Problem P_h possesses a (not necessarily unique) solution,[1] so existence is not at issue here. The goal instead is to identify the minimizers of P_h, and, what is more important, to study the asymptotic behavior for small h.

[1] Cf. Morrey [9], Theorems 1.9.1 and 1.10.1.

3. Results.

Let $n = 1$ and let Ω be the interval $(0,1)$. Then the solutions of P_0 with minimal interface are the two solutions involving a single transition between phases; namely, the function

$$u_0(x) = u_1, \quad 0 < x < V, \qquad (3.1)$$
$$u_0(x) = u_2, \quad V < x < 1$$

and its *reversal* $u_0(1-x)$. (Here V is given by (1.4).) In view of our previous discussion (Section 1), we expect these solutions to be physically preferred in the sense that they, and only they, are limits of solutions u_h of P_h. The following results (a) - (d) of Carr, Gurtin, and Slemrod [10] show, among other things, that this is indeed the case:

(a) All local minimizers of P_h are strictly monotone.[1]

(b) For h small, P_h has exactly two solutions, and one is the reversal of the other.

(c) If u_h denotes the increasing solution, and if u_0 is defined by (3.1), then, for $x \neq V$, $u_h(x)$ approaches $u_0(x)$ as h approaches zero.[2]

(d) For h small,

$$E_h(u_h) = e_h + O(\exp[-C/h]), \qquad e_h = Kh, \qquad (3.2)$$
$$\mu_h = O(\exp[-C/h]),$$

where $C,K > 0$ are constants with K the integral of $2\sqrt{W}$ from u_1 to u_2, while μ_h is the chemical potential corresponding to u_h.

One possible definition of interfacial energy is the difference between the actual energy $E_h(u_h)$ and the energy $E_0(u_0)$ which neglects interfacial effects. Since our normalization (1.3) renders $E_0(u_0)$ zero, (3.2) allows us to interpret e_h as **interfacial energy**,[3] at least asymptotically.

For $n > 1$, Gurtin and Matano [16] have obtained theorems analogous to (a), one of the simpler results being:

(e) For a (not necessarily circular) cylinder all local minimizers are monotone in the axial direction.

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[1] Cf. Chafee [11], Casten and Holland [12], and Matano [13]; the first three authors prove that for $n = 1$ all *unconstrained* local minimizers are constant; Matano generalizes this result to arbitrary n, but convex Ω.

[2] Cf. also Novick-Cohen and Segel [14], Alikakos and Shaing [15].

[3] Cahn and Hilliard [6] show that e_h gives the interfacial energy exactly when Ω is the entire real line.

They also show that:
(f) For $\Omega = D \times G$ (or $\Omega = D$) with D convex and sufficiently small, the solutions of the Euler-Lagrange equation and natural boundary condition are constant on each cross-section parallel to D.

Questions.
(1) What can be said about *local* minimizers of P_h as h approaches zero.
(2) Suppose the term $h^2|\text{grad}u|^2$ in (2.1) is replaced by the more general[1] "regularization" $g(u,h\text{grad}u)$, $g(u,0) = 0$. To what extent does the asymptotic behavior (for h small) depend on g?

[1] Cf. Maddocks and Parry [17], who introduce a regularization of this form for the unconstrained problem.

4. Conjectures for $n > 1$.

Guided by the results discussed in Section 3, I recently[1] offered the conjectures (C1) - (C3) listed below.

(C1)[2] The limits, as h approaches zero, of solutions of P_h are exactly the minimal interface solutions of P_0.

To state (C2) and (C3) succintly:

(i) Let u_0 denote a minimal-interface solution of P_0, and let $a(u_0)$ denote the interfacial area (cf. (1.7)) and $\mathfrak{k}$ the sum of principal curvatures of the associated interface, with $\mathfrak{k}$ counted positive when the center of curvature lies toward the phase 1 region.

(ii) For each h, let u_h be a solution of P_h that converges to u_0 as h approaches zero, and let μ_h denote the chemical potential of u_h.

(iii) Let e_h denote the (one-dimensional) interfacial energy (3.2).

Then the remaining conjectures are, for h small:

(C2)[3] $\quad E_h(u_h) \approx a(u_0)e_h$.

(C3) $\quad \mu_h \approx -\mathfrak{k}e_h/(u_2 - u_1)$. $\qquad$ (4.1)

The formula (4.1), often referred to as the Gibbs-Thompson relation[4], asserts that the chemical potential differs from the coarse-grain chemical potential ($\mu = 0$) by an amount proportional to the mean curvature of the interface.

The motivation behind (C3) is contained in the following *strictly formal* argument (which hopefully might form the basis of a proof). Consider Ω in $\mathbf{R}^2$. Then granted (C1), for small h the transition from u_1 to u_2 should occur over thin interfacial regions lying between concentric circular arcs. (In $\mathbf{R}^2$ minimal interfaces are arcs of circles.) Near such a region, but away from $\partial\Omega$, the solution should be approximately cylindrically-symmetric. Assuming it is, then the Euler-Lagrange equation (2.2) becomes

$$\mu_h = W'(u) - 2h^2(u_{rr} + r^{-1}u_r), \qquad (4.2)$$

where r denotes the radial coordinate and $u_r = \partial u/\partial r$, etc. Let $r = R$

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[1](C1) is contained in [18] and (C2) with (C1) were given at the American Mathematical Society meeting in Minneapolis in November 1984; (C3) was presented at the workshop on Metastability and Incompletely Posed Problems in Minneapolis in May, 1984. Subsequently, Kohn and Sternberg, and Modica, in private communications, have asserted proofs of (C1) and (C2) using as a basis work of Modica and Mortola (cf. [19]). The conjecture (C3) remains open.

[2]Cf. [8] for an analogous result within a theory that directly penalizes a sharp interface.

[3]Van der Waals himself asserted that (cf. [5], p. 201): "It will not be without interest to show that the two apparently contradictory hypotheses lead to values of the same order of magnitude for the capillary tension and energy." (The contradictory hypotheses being the classical assumption of an abrupt interface and the smooth transition of van der Waals.)

[4]Cf., e.g., Mullins and Sekerka [20], eqt. (8).

denote the approximate location of the interfacial region. Away from the interface u should be approximately constant. Granted this, choose r_1, r_2 such that

$$u_r(r_i) \approx 0, \quad u(r_i) \approx u_i,$$

and assume that $r_1 < R < r_2$. (The analysis for $r_2 < R < r_1$ is similar.) Then, if we multiply (4.2) by u_r and integrate from r_1 to r_2, we conclude, using (1.3), that

$$\mu_h(u_2 - u_1) \approx -(2h^2/R)\|u_r\|^2,$$

with $\|\cdot\|$ the $L^2(r_1,r_2)$ norm. We estimate this norm using the corresponding estimate of [10] (p. 350) for Ω an interval:

$$\|u_r\|^2 \approx K/(2h).$$

Since $R = \kappa^{-1}$, the last two estimates lead to the desired conclusion (4.1).

5. Inclusion of boundary energy.

Problem P_h neglects the contact energy between the fluid and the container walls. For this energy Cahn [21][1] proposes adding the boundary term

$$\int_{\partial\Omega} b(u), \tag{5.1}$$

with $b(z)$ the contact energy, per unit area, between the fluid and the vessel when the density is z. Without contact energy the interfacial energy between phases is[2] $O(h)$ for small h, and this suggests replacing b by hw with w fixed. We are therefore led to the functional

$$T_h(u) = \int_{\Omega} \{W(u) + h^2|\text{grad}u|^2\} + h\int_{\partial\Omega} w(u), \tag{5.2}$$

and to the problem:

(PB_h) Minimize $T_h(u)$ over the class of all sufficiently regular density distributions u that satisfy the constraint (1.1).

This problem is completely open. One would generally not expect existence,[3] but it would be important to answer the following:[4]

Questions:

(1) What is the lower semi-continuous envelope of the functional T_h over an appropriate space of constrained density fields?

(2) In situations for which PB_h has a solution for all small h, do solutions have limits as h tends to zero, and if so do the limits satisfy an associated variational principle?

I have a conjecture appropriate to Question 2. Given any subset F of Ω, let $A(F)$ and $A_1(F)$, respectively, denote the areas of the sets

$$\partial F \cap \Omega, \quad \partial F \cap \partial\Omega,$$

let β be a given constant, let

$$G(F) = A(F) + \beta A_1(F),$$

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[1] For $n = 1$.

[2] Cf. (4.2) and Footnote 1 of Section 5.

[3] Cf. Gurtin [22] for a discussion of this issue within a slightly diferent theory.

[4] Buttazzo (private communication) has investigated (1) for Problem PB_h with the term $h^2|\text{grad}u|^2$ in (5.2) replaced by $h|\text{grad}u|$.

and for each fixed V, $0 < V < 1$, consider the variational problem:

(LD) Minimize $G(F)$ subject to the constraint $\mathrm{vol}(F) = V$.

Remark. LD, known in the literature as the **liquid-drop problem**,[1] may be stated physically as follows: determine the region F occupied by an incompressible liquid drop of volume V in a container Ω with

$$\beta = \frac{\text{contact energy between drop and container walls}}{\text{surface tension of the fluid}}.$$

Definition. Let u_0 be a two-phase solution of P_0 of the form (1.5). Then u_0 **solves the liquid-drop problem** if F is a solution of LD with V given by (1.4) and

$$\beta = [w(u_1)-w(u_2)]/K.$$

(Recall that, by (3.2), Kh is the asymptotic form of the interfacial energy between phases.)

Conjecture. Let W and w be such that PB_h has a solution for all small h. Then as h approaches zero the limits of solutions of PB_h are exactly those solutions of P_0 that solve the liquid-drop problem.

Remark. For $|\beta| > 1$, one can show, using results of Massari and Pepe [1], that the liquid-drop problem does *not* have a solution for general Ω and all V, $0 < V < 1$. This leads me to conjecture that for

$$|w(u_1)-w(u_2)| > K$$

and h sufficiently small Problem PB_h does *not* have a solution for general Ω and all m.[2]

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[1] Cf., e.g., Massari and Pepe [1], Giusti [2].
[2] Cf. [22].

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