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On the Thermodynamics of Periodic Phases

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1. Introduction

We here present a theory of thermodynamical equilibrium for materials for which the free-energy density $\psi(x)$ depends not only on the concentration (or mass density) $u(x)$ and its gradient $u'(x)$, but also on $u''(x)$, the second gradient of u. We show that a broad class of such materials can exhibit equilibrium states that are periodic in a nontrivial way.

So as to be able to discuss periodic states, we drop the assumption of finite mass and volume usually made in theories of equilibrium and consider unidimensional bodies of *infinite extent*. Here, the set S of *states* will be a set of measurable functions u from $\mathbb{R}$ to $\mathbb{R}$ for which the *average value*,

$$<u> := \lim_{X\to\infty} \frac{1}{2X} \int_{x_0-X}^{x_0+X} u(x)\, dx \ , \tag{1.1}$$

is finite and independent of x_0.# We refer to the value $u(x)$, of a state u at a point x as the

If $u(\cdot)$ is *bounded* and measurable, and *if* the limit in (1.1) exists for a value of x_0, then that limit exists for all x_0 and is independent of x_0.

concentration at x and to $<u>$ as the *average concentration*. We do not treat variations in temperature. A state u determines a (Helmholtz) *free-energy field* ψ, and for the

free-energy density at a point x we write $\psi(x)$, or $\psi_u(x)$ if we wish to emphasize the dependence of the function ψ on the function u. The material of which the body is composed is characterized by the mapping $u \mapsto \psi_u$. Here this mapping is determined by a continuously differentiable function $\tilde{\psi}$ from $D = \mathbb{R}^{N+1}$ into $\mathbb{R}$, where N is the *order* of the material. For *Gibbsian* or *zeroth-order* materials, D is $\mathbb{R}$, and $\tilde{\psi}$ gives the free-energy density at x in the state u as a function of the value of the concentration at x, i.e.,

$$\psi_u(x) = \tilde{\psi}(u(x)), \qquad x \in \mathbb{R}. \tag{1.2}$$

For an Nth order material, $\tilde{\psi}$ gives $\psi_u(x)$ as a function of $u(x)$ and the first N derivatives of u at x, namely $u'(x),\ldots,u^{(N)}(x)$.# Thus, for *first-order* materials, or materials of

For simplicity of analysis we take the codomain of states u to be all of $\mathbb{R}$ and the domain of $\tilde{\psi}$ to be $\mathbb{R}^{N+1}$, albeit concentration (i.e., mass density) is never negative. Without great difficulty our results can be shown to hold when the set S of states u is restricted to those which are everywhere positive, provided appropriate growth conditions be assumed for the functions $\alpha_0 \mapsto \psi(\alpha_0, \alpha_1, \ldots, \alpha_N)$ as $\alpha_0 \to 0+$.

Van der Waals type,

$$\psi_u(x) = \tilde{\psi}(u(x), u'(x)), \qquad x \in \mathbb{R}, \tag{1.3}$$

while for *second-order* materials, the main subject of this paper,

$$\psi_u(x) = \tilde{\psi}(u(x), u'(x), u''(x)) , \qquad x \in \mathbb{R} . \tag{1.4}$$

We shall follow the general approach of Gibbs to thermostatics and say that a state u is one of *equilibrium* if it minimizes, in a sense to be explained below, an average of the free energy subject to appropriate constraints on the fields with which u is compared.

For each material, depending on its order N and the function $\tilde{\psi}$, there is a set $W(\tilde{\psi})$ of functions u in S, with $u^{(N-1)}$ locally absolutely continuous (in the case $N \geq 1$), for which ψ_u is in the class of locally Lebesgue-integrable functions from $\mathbb{R}$ to $\mathbb{R}$, and for which the *mean value*,#

We use the expressions "mean value" and "average value" to distinguish between $[\psi_u]$ and $<\psi_u>$ defined in equations (1.5) and (1.7).

$$[\psi_u] := \liminf_{X \to \infty} \frac{1}{2X} \int_{x_0 - X}^{x_0 + X} \psi_u(x)\, dx , \tag{1.5}$$

is finite and independent of x_0. We call $[\psi_u]$ the *mean free energy of the state u*. Whenever

u is in $W(\tilde{\psi})$ there is a state v for which#

Lemmata 2.1 and 2.2 give broad generalizations of this observation.

(*i*)
$$<\mathrm{v}> = <u> , \tag{1.6}$$

(*ii*) ψ_{v} has an *average value*, i.e.,

$$<\psi_{\mathrm{v}}> := \lim_{X\to\infty} \frac{1}{2X} \int_{x_0-X}^{x_0+X} \psi_{\mathrm{v}}(x)\, dx , \tag{1.7}$$

is a real number independent of x_0, and

(*iii*)
$$<\psi_{\mathrm{v}}> = [\psi_u] . \tag{1.8}$$

Thus, for each state u in $W(\tilde{\psi})$ there is another state v that has the same average concentration as u and gives rise to an average free energy equal to the mean free energy of u; if, however, the state u is such that ψ_u does not have an average value in the sense of (1.7), but only a mean value in the sense of (1.5), there is no guarantee that v can be chosen so as to be also close to u in a natural metric on $W(\tilde{\psi})$.

For each a we write $U(a)$ for the set of states for which $[\psi_u]$ is independent of x_0 and the average value of the concentration is a, i.e.,

$$U(a) := \{ u \in W(\tilde{\psi}) \mid <u> = a \} , \tag{1.9}$$

and we write $\Psi(a)$ for the infimum of $[\psi_u]$ for such states:

$$\Psi(a) := \inf \{ \ [\psi_u] \mid u \in U(a) \ \} \ . \tag{1.10}$$

Assumptions to be made below# about $\tilde{\psi}$ will imply that $\Psi(a)$ is finite. A function u^* in

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The assumptions are growth conditions for $\tilde{\psi}$. For the important case of second-order materials, the assumptions are stated at the beginning of Section 3. For zeroth-order and first-order materials, the "standard assumption" (stated later in this Introduction) and non-negativity of ν in (1.24) insure that $\Psi(a)$ is finite for each a. A condition sufficient for general materials of order $N \geq 1$ is given in Lemma 2.3.

$U(a)$ is called an *equilibrium state* (with average concentration a) if

$$[\psi_{u^*}] = \Psi(a), \tag{1.11}$$

i.e., if it minimizes the mean free energy subject to the constraint $\langle u \rangle = a$.

The main problem of our subject is that of characterizing equilibrium states u^* and the *equilibrium response function* Ψ.

The theories of equilibrium for zeroth- and first-order materials are highly developed subjects. The classical results for such materials are for bodies of finite extent, but rest on methods that can be employed to describe equilibrium states of unbounded bodies. To have a background against which one can view the corresponding theory of second-order materials, in this introduction we shall discuss briefly the equilibrium of bodies of infinite extent composed of zeroth- and first-order materials. Later in the paper we shall show that a principal difference between certain second-order materials and the classical lower-order materials is that for the second-order materials nontrivial periodic equilibrium states play a central role in the relation between the functions $\tilde{\psi}$ and Ψ. It is possible that the theory of such second-order materials may supply insight into periodic layering phenomena observed in various types of mixtures, such as concentrated soap solutions and metallic alloys, but in this paper we prefer not to refer to applications. Before applications can be considered, the mathematical implications of the theory must be examined. We hope that this paper will convince the reader that the theory of second-order materials is not just a perturbation of the more familiar theories of lower-order materials, but is instead a rich subject that raises interesting mathematical issues.

For a general Nth order material, the function $\tilde{\psi}_0$, defined in terms of $\tilde{\psi}$ by

$$\tilde{\psi}_0(u) = \tilde{\psi}(u,0,\ldots,0) \ , \qquad u \in \mathbb{R} \ , \tag{1.12}$$

is called the *homogeneous response function* for free energy. For a zeroth-order material $\tilde{\psi}_0$ is the same as $\tilde{\psi}$, while for the first- and second-order materials $\tilde{\psi}_0(u) = \tilde{\psi}(u,0)$

and $\tilde{\psi}_0(u) = \tilde{\psi}(u,0,0)$, respectively. As $\tilde{\psi}$ is assumed to be continuously differentiable on $D = \mathbb{R}^{N+1}$, $\tilde{\psi}_0$ is continuously differentiable on $\mathbb{R}$. A point v in $\mathbb{R}$ is a *support point* for $\tilde{\psi}_0$ if

$$\tilde{\psi}_0(u) \geq \tilde{\psi}_0(\mathrm{v}) + \tilde{\psi}_0'(\mathrm{v})(u-\mathrm{v}), \quad \text{for all } u \in \mathbb{R}; \tag{1.13}$$

v is an *exposed point* for $\tilde{\psi}_0$ if, in addition,

$$\tilde{\psi}_0(u) > \tilde{\psi}_0(\mathrm{v}) + \tilde{\psi}_0'(\mathrm{v})(u-\mathrm{v}), \quad \text{when } u \neq \mathrm{v}\ . \tag{1.14}$$

As is common practice in the thermodynamical literature, we assume here that $\tilde{\psi}_0$ obeys the following **standard assumption**.– Either *(i)* or *(ii)*, below, holds:

(i) $\tilde{\psi}_0$ is *strictly convex* on $\mathbb{R}$; i.e., $\tilde{\psi}_0'$ is strictly increasing on $\mathbb{R}$ (or, equivalently, every point in $\mathbb{R}$ is an exposed point of $\tilde{\psi}_0$);

(ii) there are two numbers u_1, u_2 with $u_1 < u_2$ such that $\tilde{\psi}_0$ is strictly convex on $I_1 = (-\infty, u_1)$ and $I_2 = (u_2, \infty)$ and is strictly concave on (u_1, u_2), i.e., $\tilde{\psi}_0'$ is strictly increasing on I_1 and I_2 and strictly decreasing on (u_1, u_2).

In case (*ii*) there are precisely two numbers, u_α, u_β, with $u_\alpha < u_\beta$ such that

$$\tilde{\psi}_0'(u_\alpha) = \tilde{\psi}_0'(u_\beta) = \frac{\tilde{\psi}_0(u_\beta) - \tilde{\psi}_0(u_\alpha)}{u_\beta - u_\alpha}\ , \tag{1.15}$$

and each point u with $u < u_\alpha$ or $u > u_\beta$ is an exposed point for $\tilde{\psi}_0$; u_α and u_β are support points for $\tilde{\psi}_0$.

Zeroth-Order Materials

Consider now a Gibbsian material, so that $\tilde{\psi}_0 = \tilde{\psi}$. Suppose first that a is a support point for $\tilde{\psi}_0$. Then for each u in S,

$$\tilde{\psi}(u(x)) \geq \tilde{\psi}(a) + \tilde{\psi}'(a)(u(x)-a) \ , \quad \text{for all } x \in \mathbb{R} \ , \tag{1.16}$$

and hence for each u in $U(a)$,

$$[\psi_u] \geq \tilde{\psi}(a) + \tilde{\psi}'(a) < u - a > \ = \ \tilde{\psi}(a) \ . \tag{1.17}$$

Thus, for u in $U(a)$, $[\psi_u] \geq \tilde{\psi}(a) = \tilde{\psi}_0(a)$, and, of course, if $u \equiv a$, $[\psi_u] = \tilde{\psi}(a) = \tilde{\psi}_0(a)$. Hence, for a Gibbsian material, if a is a support point for $\tilde{\psi}_0$, the homogeneous state $u \equiv a$ is a state of equilibrium.

For an *exposed point* a this last statement can be strengthened to the assertion that each equilibrium state u^* in $U(a)$ is nearly the same as the constant field $u \equiv a$ in the sense that

$$[\,|u^* - a|\,] = 0 \ . \tag{1.18}$$

In fact, if a is an exposed point, it is easily seen that for each $\delta > 0$ an equilibrium state u^* in $U(a)$ must satisfy $[\,|u^* - a|_{(\delta)}\,] = 0$, where $|r|_{(\delta)} = |r|$ if $|r| > \delta$ and $|r|_{(\delta)} = 0$ if $|r| \le \delta$, and it then follows that $[\,|u^* - a|\,] \le \delta$ for all $\delta > 0$.

For Gibbsian materials obeying the standard assumption, when $u \equiv a$ is an equilibrium state, a is a support point of $\tilde{\psi}_0$. To see this (and much more), it suffices to consider only case *(ii)* of the standard assumption with a between u_α and u_β, because the values of a obeying

$$a = \theta u_\alpha + (1-\theta)u_\beta \qquad (0 < \theta < 1)\ , \tag{1.19}$$

are the only values that are not support points for $\tilde{\psi}_0$. In Gibbs' classical theory of bodies of finite extent [1873][1875], when a is as in (1.19), each equilibrium state u^* with average value a equals u_α on fraction θ of the total mass and u_β on the remaining fraction, $1-\theta$. In the present theory of bodies of infinite extent, the following assertions hold: For each measurable subset A of $\mathbb{R}$ whose characteristic function χ_A obeys the relation

$$\theta = \lim_{X\to\infty} \frac{1}{2X} \int_{x_0-X}^{x_0+X} \chi_A(x)\, dx \tag{1.20}$$

for some (and hence every) choice of x_0, the function

$$u^* = u_\alpha \chi_A + u_\beta \chi_B\ , \tag{1.21}$$

with B the complement of A, is an equilibrium state for which the average concentration is a and the mean free energy $[\psi_{u^*}]$ obeys

$$[\psi_{u^*}] = <\psi_{u^*}> = \Psi(a) = \theta\tilde{\psi}(u_\alpha) + (1-\theta)\,\tilde{\psi}(u_\beta) < \tilde{\psi}(a)\ . \qquad (1.22)$$

Moreover, every equilibrium state u_* with $<u_*> = a$ is "nearly the same" as some state u^* obeying (1.21) with A as in (1.20), in the sense that,

$$[\,|u^* - u_*|\,] = 0\,. \qquad (1.23)$$

This implies that if a is not a support point for $\tilde{\psi}_0$, then $u \equiv a$ is not an equilibrium state. From the observations just made, particularly the relations (1.22), we may conclude that, for a Gibbsian material obeying the standard assumption, the equilibrium response function Ψ is conv $\tilde{\psi}_0$.[#] In fact, this conclusion holds under

[#] conv $\tilde{\psi}_0$, the "convex envelope" of $\tilde{\psi}_0$, is the largest convex function that nowhere exceeds $\tilde{\psi}_0$.

hypotheses on $\tilde{\psi}_0$ that are far more general than the standard assumption.

It should be noted that when the average concentration a is not an exposed point or a limit of exposed points for $\tilde{\psi}_0$, each equilibrium state u^* of the Gibbsian material with $<u^*> = a$ is nonuniform and, under the standard assumption or appropriate generalizations thereof, is a state with two phases;# the thermodynamics of zeroth-order materials gives no

Here $u^*(x)$ equals u_α in one phase and u_β in the other.

information about the, in general many, boundaries between the regions of constant concentration.

For materials of order $N \geq 1$ we shall take S to be the set of functions u from $\mathbb{R}$ to $\mathbb{R}$ for which $u, u', u'', \ldots, u^{(N-1)}$ are in $L^\infty(\mathbb{R})$ and are locally absolutely continuous and for which u has a finite average value $<u>$ given by (1.1). Once we assume u to be essentially bounded, the limit (1.1) is independent of x_0.

First-Order Materials

The commonly considered examples of first-order materials are those for which $\tilde{\psi}$ has the form

$$\tilde{\psi}(u,u') = \tilde{\psi}_0(u) + \frac{1}{2}\nu(u)(u')^2 \ , \tag{1.24}$$

where $\tilde{\psi}_0$ and ν are continuously differentiable functions with $\tilde{\psi}_0$ obeying the standard assumption and ν everywhere positive.#

If $\nu(u)$ in (1.24) were negative for an interval of values of u, there would be no equilibrium states for *any* specified value of the average concentration a. It is usual to assume that ν is a positive constant.

If we write Ψ_1 for the equilibrium response function of the material defined by (1.24) and Ψ_0 for the equilibrium response function of the zeroth-order material with $\tilde{\psi}$ equal to the function $\tilde{\psi}_0$ in (1.24), then, clearly, for all a in $\mathbb{R}$,

$$\Psi_0(a) \leq \Psi_1(a) \ . \tag{1.25}$$

Let a be given, and let u belong to the set $U(a)$ for a first-order material obeying (1.24); by (1.25), if $[\psi_u] = \Psi_0(a)$, then u is an equilibrium state of the first-order material. Here, as for zeroth-order materials, the constant function $u \equiv a$ is an equilibrium state if and only if a is a support point for $\tilde{\psi}_0$. Moreover, as ν is positive and $\tilde{\psi}_0$ obeys the standard assumption, one can again show that when a is an exposed point (1.18) is a necessary (but not sufficient) condition for a state u^* in $U(a)$ to be an equilibrium state. Consequently, if a is an exposed point for $\tilde{\psi}_0$ the first-order material has no nontrivial periodic equilibrium fields with average value a. In fact, one can show that when $\tilde{\psi}_0$ obeys the standard assumption there are no nontrivial periodic equilibrium states, and in case (*ii*) of the standard assumption, for a in (u_α, u_β), i.e., when a is not a support point for $\tilde{\psi}_0$, there are *no* periodic equilibrium states, not even constant ones.

We consider now case *(ii)* of the standard assumption and give some examples of equilibrium states with average concentration a in (u_α, u_β).

When

$$a = \tfrac{1}{2}(u_\alpha + u_\beta) \ , \tag{1.26}$$

so that $\theta = \frac{1}{2}$ in (1.19), any non-constant function u^* with

$$\tfrac{1}{2}\,\nu(u^*)(u^{*\prime})^2 \;=\; \tilde{\psi}_0(u^*) \;-\; \tilde{\psi}_0'(u_\alpha)(u^* - u_\alpha) \tag{1.27}$$

i.e., obeying

$$\pm \int_{(u_\alpha + u_\beta)/2}^{u^*(x)} \left[\tfrac{2}{\nu(u)}\left(\tilde{\psi}_0(u) - \tilde{\psi}_0'(u_\alpha)(u - u_\alpha)\right)\right]^{-1/2} du = x - x_0 \tag{1.28}$$

with x_0 arbitrary, gives an equilibrium state with $<u^*> = a$. The function u_*^+, defined by (1.28) with the choice of + on the left, is an increasing function that equals a at x_0 and approaches u_β as $x \to \infty$ and u_α as $x \to -\infty$. On the other hand, the function u_*^- obtained by choosing − on the left in (1.28) is a decreasing function that approaches u_α as $x \to \infty$ and u_β as $x \to -\infty$.#

If $u(x)$ be identified with the stretch at axial location x in a long fiber, then the functions u_*^+ and u_*^- describe the equilibrium configurations called "fully developed draws" in a theory [1983] [1985] [1988] of elastic materials susceptible to cold drawing. In that theory the present $\tilde{\psi}_0'(u)$ is equal to the tension (per unit of undeformed cross-sectional area) the fiber would be bearing if it were homogeneously stretched by amount u, and $\nu(u)$ is determined when $\tilde{\psi}_0'(u)$ is known, i.e., $\nu(u) = \frac{1}{32} D^2 \tilde{\psi}_0'(u) u (u^3 - 1)^{-1}$, with D the diameter of the unstretched fiber.

If θ in (1.19) is not 1/2, there are again equilibrium states with average concentration a, but they are not monotonic in x; nor are they constant or periodic. To see how one such class of equilibrium states can be constructed,[#] let $I_n = [a_n, b_n]$, with

[#] As will be clear from arguments given in Section 2, the equilibrium fields constructed here can be replaced by others. The present construction uses the functions u_*^+ and u_*^- which are familiar in theories of the structure of interfaces between stable homogeneous phases with densities u_α, u_β.

$n = 0, \pm 1, \pm 2, \ldots$, be closed intervals whose length $b_n - a_n$ grows without bound as $n \to +\infty$ and as $n \to -\infty$; suppose that I_n precedes I_{n+1} with unit distance between the two intervals, i.e., that $a_{n+1} = b_n + 1$; and let $x_0(n)$ be the point in I_n such that

$$\frac{x_0(n) - a_n}{a_n - b_n} = \theta, \quad \text{for even } n, \tag{1.29a}$$

$$\frac{b_n - x_0(n)}{a_n - b_n} = \theta, \quad \text{for odd } n. \tag{1.29b}$$

Now, let u^* be the continuous function on $\mathbb{R}$ defined so that

(1) on I_n, n even, $u^* = u_*^+$ with u_*^+ the increasing function given by (1.28) with

$x_0 = x_0(n)$;

(2) on I_n, n odd, $u^* = u_*^-$ with u_*^- the decreasing function given by (1.28) with

$x_0 = x_0(n)$;

(3) on the unit interval separating I_n and I_{n+1}, u^* is an affine function.

Such a function u^* is piecewise continuously differentiable on IR and possesses a bounded first derivative. Moreover, u^* has average value a and is an equilibrium field. For a given a in (u_α, u_β), the class of equilibrium fields that can be constructed by this procedure is by no means exhaustive.

The construction just given makes it easy to see that the equilibrium response functions Ψ_1, for a first-order material obeying (1.24), and Ψ_0, for the zeroth-order material with the same homogeneous response function $\tilde{\psi}_0$, are equal and given by:

$$\Psi_1 = \Psi_0 = \mathrm{conv}\,\tilde{\psi}_0 \,. \tag{1.30}$$

Preliminary Remarks on Second-Order Materials

For materials of order two, we have frequent occasion to consider functions $\tilde{\varphi}$ related to $\tilde{\psi}$ by an equation of the form,

$$\tilde{\varphi}(u,u',u'') = \tilde{\psi}(u,u',u'') - \lambda u \ , \tag{1.31}$$

in which λ is a constant. For each λ, the set $W(\tilde{\varphi})$ is the same as $W(\tilde{\psi})$, and for every u in $W(\tilde{\varphi})$, $[\varphi_u]$, given by (1.5) with

$$\varphi_u(x) = \tilde{\varphi}(u(x),u'(x),u''(x)) \ , \tag{1.32}$$

is related to $[\psi_u]$ by

$$[\varphi_u] = [\psi_u] - \lambda <u> . \tag{1.33}$$

We write $\Phi(\lambda)$ for the infimum of $[\varphi_u]$ as u varies over all $W(\tilde{\psi})$ without constraint on the average value of u:

$$\Phi(\lambda) = \inf \{ [\varphi_u] \mid u \in W(\tilde{\psi}) \} . \tag{1.34}$$

Suppose now that this infimum is attained at a function u_λ, i.e., that

$$[\varphi_{u_\lambda}] = \Phi(\lambda) . \tag{1.35}$$

Then, if we put $a_\lambda = <u_\lambda>$, u_λ certainly minimizes $[\varphi_u]$ over the set of u in $W(\tilde{\psi})$ with $<u> = a_\lambda$, or, by (1.33),

$$[\varphi_{u_\lambda}] = \inf \{ [\psi_u] - \lambda a_\lambda \mid u \in W(\tilde{\psi}), \ <u> = a_\lambda \} \ , \tag{1.36}$$

and hence u_λ minimizes $[\psi_u]$ over $U(a_\lambda)$:

$$[\psi_{u_\lambda}] = \inf \{ [\psi_u] \mid u \in U(a_\lambda) \} = \Psi(a_\lambda) . \tag{1.37}$$

Although we have this expected relation between the problem of minimizing $[\varphi_u]$ without a constraint on $\langle u \rangle$ and that of minimizing $[\psi_u]$ with $\langle u \rangle$ preassigned, even in cases in which one can show that the former problem has a solution, it is not an elementary matter to show that the latter problem has a solution for an arbitrarily preassigned value of $\langle u \rangle$. Nevertheless, it is convenient to study the former and apparently easier problem.

When $\tilde{\psi}$ has the form,

$$\tilde{\psi}(u, u', u'') = \tilde{\psi}_0(u) - b(u')^2 + c(u'')^2 \tag{1.38}$$

with b a positive constant and $\tilde{\psi}_0$ a twice-differentiable function obeying the standard assumption, existence of a minimizer for $[\varphi_u] = [\psi_u - \lambda u]$ on the set $W(\tilde{\psi})$ requires that c be positive. In such a case, one expects that, for a broad class of functions $\tilde{\psi}_0$, $[\varphi_u]$ will have a minimum on $W(\tilde{\psi})$ but this minimum will not be attained at a constant field u^* if c is sufficiently small or b sufficiently large. To discuss the implications of results of Leizarowitz and Mizel [1989] that shed light on the matter, let us suppose that (1.38) holds with

$$b > 0, \qquad c > 0, \tag{1.39}$$

and that $\tilde{\psi}_0$ obeys the standard assumption as well as the growth condition

$$\tilde{\psi}_0(u) \geq \beta|u|^{\alpha} - d, \qquad (\alpha > 2,\ \beta > 0,\ d > 0). \tag{1.40}$$

Arguments given by Leizarowitz and Mizel show that for a class of second-order materials that includes those obeying (1.38)-(1.40), the infimum (1.34) is finite and is attained at periodic states u_λ whose free energy is not raised by perturbations on intervals of finite length, *i.e.*, for which

$$\int_{-\infty}^{\infty} [\, \psi_{u_\lambda + \mathrm{v}}(x) - \psi_{u_\lambda}(x) \,]\, dx \geq 0 \tag{1.41}$$

for all continuously differentiable functions v of compact support in $\mathbb{R}$ for which v′ is absolutely continuous. Moreover, when b exceeds a critical value which depends on λ, the minimizers u_λ are not constant functions.

Note: as $\tilde{\psi}_0$ is here twice-differentiable, once it is assumed that $\tilde{\psi}_0$ obeys the standard assumption it follows that $\tilde{\psi}_0''$ is positive on a set that is everywhere dense either in $\mathbb{R}$ or in the complement in $\mathbb{R}$ of a bounded interval $[u_1, u_2]$. If this property of $\tilde{\psi}_0$ is slightly strengthened by assuming not only the standard assumption but also that there is a bounded interval I such that for u outside of I, $\tilde{\psi}''(u) > \varepsilon\,|u|^{\delta}$ for some $\varepsilon > 0$, $\delta > 0$, then the growth condition (1.40) is automatically satisfied.

In this paper we shall show that, for a broad class of second-order materials# that

The class is defined by the relations (3.1) – (3.4).

includes those that obey (1.38) – (1.40), the infimum, $\Psi_2(a)$, of $[\psi_u]$ over $U(a)$ is finite and is attained for each a in $\mathbb{R}$, and the resulting equilibrium response function Ψ_2 is a convex function from $\mathbb{R}$ into $\mathbb{R}$ with

$$\Psi_2 \leq \operatorname{conv} \tilde{\psi}_0 . \tag{1.42}$$

Furthermore, we shall show that, for each compact interval I, if (1.38) – (1.40) holds#

A generalization of (1.38) – (1.40) that suffices for (1.43) is given in the paragraph containing (3.5).

with b sufficiently large, (1.42) becomes

$$\Psi_2(a) < \operatorname{conv} \tilde{\psi}_0(a), \quad \text{for all } a \in I , \tag{1.43}$$

and this implies that there are no homogeneous equilibrium states with average concentration a in I. However, for sufficiently large a, $\Psi_2(a) = \tilde{\psi}_0(a)$. We shall show further that, for such second-order materials, when a is an exposed point or a limit of exposed points of Ψ_2, among the equilibrium states with average value a are states which form periodic phases in the sense that for them u is a periodic function on $\mathbb{R}$,# whereas for

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This is the principal content of Lemmata 3.1 and 3.2.

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the other values of a, *i.e.*, for values that are not extreme points of the function Ψ_2, among the equilibrium states in $U(a)$ are states that can be regarded as asymptotically twice-periodic mixtures of pairs of periodic states.#

Lemma 3.3.

Before presenting our theory of second-order materials in Section 3, we derive, in Section 2, some general properties of materials of order one or higher, such as the convexity of Ψ, and we develop a method for showing that Ψ is finite-valued. It is there that we introduce the definition that renders precise the concept of a "mixture of states"# and employ that definition to show that for each u in $W(\tilde{\psi})$ there is a v for

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Definition 2.2.

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which (1.6) – (1.8) hold.

The main results for second-order materials are brought together in Theorems 3.1 and 3.2. Theorem 3.1 summarizes results proven in Lemmata 3.1 – 3.3 about the existence of periodic and asymptotically-twice periodic equilibrium states with specified values of a. In Theorem 3.2, which is applicable to materials of order $N \geq 2$, we give a general condition on $\tilde{\psi}$ under which conv $\tilde{\psi}_0$ exceeds Ψ.

The present theory suggests a procedure of homogenization which we discuss in a preliminary way in Section 4. The procedure associates with bounded functions u on the real line Young measures obtained as limits for small ε of the functions u_ε defined on $I_1 = [-1, 1]$ by the rescaling operation: $u_\varepsilon(y) = u(y/\varepsilon)$. In some important cases, e.g., when the function u is periodic or represents an asymptotically twice-periodic mixture of states, the limit of u_ε as $\varepsilon \rightarrow 0$ is fiber-constant, *i.e.*, is a Young measure that is independent of y in I_1. When this is the case, we say that u is *pseudoperiodic*. It can be shown that the class of pseudoperiodic functions includes those that are almost periodic in the sense of Besicovitch. Theorem 4.1, whose proof will be presented elsewhere, provides conditions on the function $\tilde{\psi}$ for materials of order $N \geq 2$ sufficient to guarantee that for each a in $\mathbb{R}$ there is a pseudoperiodic equilibrium state u_a with $\langle u_a \rangle = a$.

2. General Observations

We here derive general properties of materials of order $N \geq 1$. As mentioned in the Introduction, we take the set S of states to be the set of functions u from $\mathbb{R}$ to $\mathbb{R}$ for which $u, u', \ldots, u^{(N-1)}$ are locally absolutely continuous and are in $L^\infty(\mathbb{R})$, and for which u has a finite average value $\langle u \rangle$. Recall that $\tilde{\psi}$ is a continuously differentiable function from $\mathbb{R}^{N+1}$ to $\mathbb{R}$ and that we write $W(\tilde{\psi})$ for the set of u in S for which ψ_u is locally Lebesgue-integrable and $[\,\psi_u\,]$, defined in (1.5), is finite and independent of x_0. We again define $U(a)$ and $\Psi(a)$ by (1.9) and (1.10). Throughout most of this section we shall assume that, at least for one a in $\mathbb{R}$, say a_o, $\Psi(a_o) > -\infty$. Lemma 2.3, presented at the end of the section, implies that Ψ is real-valued on $\mathbb{R}$ for $N = 2$ under hypotheses weaker than (1.38) – (1.40).

The set $W_0(\tilde{\psi})$ of functions defined in Definition 2.1 below is a subset of S containing $W(\tilde{\psi})$; $W_0(\tilde{\psi})$ need not equal $W(\tilde{\psi})$ because, even when the limit inferior seen in (1.5) is finite for some value of x_0, say $x_0 = 0$, it is not automatically independent of x_0. The set $W_0(\tilde{\psi})$, and the larger set $W^\circ(\tilde{\psi})$ of Definition 2.3, supply natural settings for demonstration of the observation summarized in equations (1.6) – (1.8).

Definition 2.1. (1) For each integer N, let $W_0(\tilde{\psi})$ be the set of measurable functions $u : \mathbb{R} \to \mathbb{R}$ for which

(*i*) $u, u', \ldots, u^{(N-1)}$ are in $L^\infty(\mathbb{R})$ and are locally absolutely continuous;

(*ii*) $\psi_u : = \tilde{\psi}(u, u', \ldots, u^{(N)})$ is locally Lebesgue-integrable;

(*iii*) $\frac{1}{2X} \int_{-X}^{X} u(x)\,dx$ has a finite limit as $X \to \infty$, and hence, by (*i*), u is in S and has an average value $<u>$ obeying (1.1) for every x_0;

(*iv*) the number,

$$[\psi_u]_0 : = \liminf_{X \to \infty} \frac{1}{2X} \int_{-X}^{X} \psi_u(x)\,dx \tag{2.1}$$

is finite.

(2) Let $W_1(\tilde{\psi})$ be the set of u in $W_0(\tilde{\psi})$ for which

(*iv*)′ there is a number $<\psi_u>$ such that

$$<\psi_u> = \lim_{X \to \infty} \frac{1}{2X} \int_{x_0-X}^{x_0+X} \psi_u(x)\,dx \tag{2.2}$$

for every x_0; of course, $<\psi_u> = [\psi_u]_0$.#

Clearly, $W_1(\tilde{\psi}) \subset W(\tilde{\psi})$.

We now state a technical definition to be employed in the proof of Lemma 2.1 below. This definition renders precise the concept of a mixture of states.

Definition 2.2. Let $\{u_m\}, m \geq 0$, be a sequence of states in $W_0(\psi)$, $\{A_m\}$ a sequence of positive real numbers, and $\{k_m\}$ a sequence of positive integers. Put

$$\alpha_{-1} = A_0/2; \qquad \alpha_m = k_m A_m + \alpha_{m-1} \text{ for } m \geq 0 \ ; \tag{2.3}$$

$$J_m = [-A_m/2,\ A_m/2] \text{ for } m \geq 0 \ ; \tag{2.4}$$

$$I_{-1} = [-A_0/2, A_0/2] \ ; \qquad I_m = (\alpha_{m-1},\ \alpha_m] \text{ for } m \geq 0 \ . \tag{2.5}$$

For $m \geq 0$, let $\hat{u}_m$ be the function on I_m defined by

$$\hat{u}_m(x) = u_m(f_m(x\text{-}\alpha_{m-1}))\ , \tag{2.6}$$

where#

For a real number s, $[s]$ is the largest integer not exceeding s.

$$f_m(x) = x - [x/A_m]A_m - A_m/2\ , \tag{2.7}$$

and hence f_m maps $\mathbb{R}$ into J_m. The *mixture* of the sequence $\{u_m\}$ (subject to $\{A_m\}$, $\{k_m\}$) is the function

$$\hat{u} = \text{Mix}\ (\{u_m\}, \{A_m\}, \{k_m\}), \tag{2.8}$$

defined on IR by

$$\hat{u}(x) = \hat{u}_m(x) \text{ for } x \text{ in } I_m, \quad m \geq 0, \tag{2.9a}$$

$$\hat{u}(x) = u_0(x) \text{ for } x \text{ in } I_{-1}, \tag{2.9b}$$

$$\hat{u}(x) = \hat{u}(x+\alpha_{m-1}+\alpha_m) \text{ for } x \text{ in } (-\alpha_m, -\alpha_{m-1}], \quad m \geq 1. \tag{2.9c}$$

It will be noticed that this construction of $\hat{u}$ does not require knowledge of the functions u_m on all of IR, for it can be implemented whenever the domain of each u_m contains the associated interval J_m defined in (2.4).

Lemma 2.1. For each u in $W_0(\tilde{\psi})$ there is a v in $W_1(\tilde{\psi})$ with

$$<\mathrm{v}> = <u>, \qquad <\psi_{\mathrm{v}}> = [\psi_u]_0. \tag{2.10}$$

Proof: Given u in $W_0(\tilde{\psi})$, let $\{X_m\}$ be an unbounded increasing sequence of positive numbers for which, as $m \to \infty$,

$$\frac{1}{2X_m} \int_{-X_m}^{X_m} \psi_u(x)\,dx \to [\psi_u]_0. \tag{2.11}$$

For each $m \geq 0$, put

$$\gamma_m := \int_{-X_m}^{X_m} |\psi_u(x)|\,dx \tag{2.12}$$

and let $\{k_m\}$ be an increasing sequence of positive integers such that, as $m \to \infty$,

$$X_{m+1} \Big/ \sum_{i=0}^{m} k_i X_i \to 0 \ , \tag{2.13a}$$

$$\gamma_{m+1} \Big/ \sum_{i=0}^{m} k_i X_i \to 0 \ . \tag{2.13b}$$

For each $m \geq 0$, let J_m be as in (2.4) with

$$A_m = 2(X_m + 1) \ , \tag{2.14}$$

and construct as follows a sequence $\{\mathrm{v}_m\}$ with v_m in $C^{N-1}(J_m)$, $m \geq 0$:

$$\mathrm{v}_m(x) = u(x) \quad \text{for } x \in [-X_m, X_m], \tag{2.15a}$$

$$\mathrm{v}_m(x) = \mathrm{v}_m'(x) = \mathrm{v}_m''(x) = \ldots = \mathrm{v}_m^{(N-1)}(x) = 0 \quad \text{for } x = \pm (X_m + 1), \tag{2.15b}$$

v_m is a polynomial of degree $2N - 1$ on $[-X_m - 1, -X_m)$ and on $(X_m, X_m + 1)$. (2.15c)

Note that v_m is fully determined by these conditions. Because

$$\sup_{x \in \mathbb{R}} \{ |u(x)|, |u'(x)|, \ldots, |u^{(N-1)}(x)| \} < \infty \ , \tag{2.16}$$

as x varies over the sets $Q_m = (X_m, X_m + 1] \cup (-X_m - 1, -X_m]$, the quantities $\mathrm{v}_m^{(N)}(x)$ have a (finite) bound that is independent of m, and hence the restrictions to Q_m of the functions ψ_{v_m} are bounded, uniformly in m. It is not difficult to verify that the function

$$\mathrm{v} = \mathrm{Mix}\,(\{\mathrm{v}_m\}, \{A_m\}, \{k_m\}) \tag{2.17}$$

obeys (2.10). To this end one should note that, because v is bounded, (2.13a) implies that the oscillations of $\frac{1}{2X} \int_{-X}^{X} \mathrm{v}(x)\,dx$ vanish as $X \to \infty$. On the other hand, (2.13b) implies not only that $\frac{1}{2X}\int_{-X}^{X}\psi_v(x)dx$ has the same property but that this lin t is unaffected by shifts of the origin of the x-axis; q.e.d.

Definition 2.3. Let $W^{\circ}(\tilde{\psi})$ be the set of measurable functions u on $\mathbb{R}$ obeying items *(i)* and *(ii)* of Definition 2.1 and the following weakened form of items *(iii)* and *(iv)*:

(w) There are two (finite) numbers, $[u]^{\circ}$ and $[\psi_u]^{\circ}$ and at least one sequence $\{X_n^{\circ}\}$ for which, as $n \to \infty$, $X_n^{\circ} \to \infty$ and both

$$\frac{1}{2X_n}\int_{-X_n^{\circ}}^{X_n^{\circ}} u(x)\,dx \to [u]^{\circ}, \qquad \frac{1}{2X_n^{\circ}}\int_{-X_n^{\circ}}^{X_n^{\circ}} \psi_u(x)\,dx \to [\psi_u]^{\circ}. \tag{2.18}$$

Clearly, $W_0(\tilde{\psi}) \subset W^{\circ}(\tilde{\psi})$, and the proof of Lemma 2.1 gives us also

Lemma 2.2. For each u in $W^{\circ}(\tilde{\psi})$ there is a v in $W_1(\tilde{\psi})$ with

$$<\mathrm{v}> = [u]^{\circ}, \qquad <\psi_{\mathrm{v}}> = [\psi_u]^{\circ}. \tag{2.19}$$

This generalization of Lemma 2.1 is employed in the proof of the following theorem giving the extension to the present theory of Gibbs' observation that, for bodies of finite extent composed of zeroth order materials, the equilibrium response function Ψ, defined in equation (1.10), is convex. The extension is not trivial, because, as we mentioned in the Introduction, there are materials (of order greater than 1) for which Ψ is *not* everywhere equal to conv $\tilde{\psi}_0$. The utility of Lemma 2.2 lies in the fact that it permits us to replace (1.10) by

$$\Psi(a) = \inf \{ [\psi_u]^\circ \mid u \in W^\circ(\psi),\ [u]^\circ = a \}. \tag{2.20}$$

We shall use also the following corollary to Lemma 2.1:

$$\Psi(a) = \inf \{ \langle\psi_u\rangle \mid u \in W_1(\psi),\ \langle u\rangle = a \}. \tag{2.21}$$

Note: (2.20) and (2.21) hold whether or not $\Psi(a)$ is finite.

Theorem 2.1. Ψ is a convex real-valued function on $\mathbb{R}$. In particular, Ψ is continuous.

Proof. We first note that as $\tilde{\psi}_0$ is real-valued, for each a in $\mathbb{R}$, $\Psi(a) < \infty$. We have assumed that there is a point $a_\circ$ at which $\Psi(a_\circ) > -\infty$; clearly, at that point, $\Psi(a_\circ)$ is a real number. Let a_1 and a_2 in $\mathbb{R}$ with $a_1 < a_2$ be given, and for a given θ in (0,1) put

$$a = \theta a_1 + (1-\theta) a_2. \tag{2.22}$$

We wish to show that

$$\Psi(a) \leq \theta\Psi(a_1) + (1-\theta)\Psi(a_2) . \tag{2.23}$$

To this end we let u_1 and u_2 be any two functions in $W_1(\tilde{\psi})$ with $<u_1> = a_1$, $<u_2> = a_2$; then, as $X \to \infty$,

$$\frac{1}{2X}\int_{-X}^{X} u_i(x)\,dx \to a_i, \qquad \frac{1}{2X}\int_{-X}^{X} \psi_{u_i}(x)\,dx \to <\psi_{u_i}>, \qquad i = 1, 2. \tag{2.24}$$

Let $\{k_m^{(1)}\}$ and $\{k_m^{(2)}\}$ be bounded increasing sequences of positive integers such that

$$\frac{k_m^{(1)}}{k_m^{(2)}} \to \frac{\theta}{1-\theta}, \tag{2.25}$$

and use these sequences to define $\{k_m\}$ by

$$k_0 = 1, \quad \text{and} \quad k_{2m-1} = k_m^{(1)}, \quad k_{2m} = k_m^{(2)}, \quad \text{for } m \geq 1. \tag{2.26}$$

With

$$A_0 = 2, \quad \text{and} \quad A_{2m} = A_{2m-1} = 2(m+1), \quad \text{for } m \geq 1 \tag{2.27}$$

define J_m by (2.4), and construct $\{\mathrm{v}_m\}$ with v_m in $C^{N-1}(J_m)$, $m \geq 0$, as follows:

$\mathrm{v}_m(x) = u_1(x)$ (if m is odd) and $= u_2(x)$ (if m is even), for $x \in [1-\frac{1}{2}A_m, \frac{1}{2}A_m-1]$, (2.28a)

$\mathrm{v}_m(x) = \mathrm{v}_m'(x) = \ldots = \mathrm{v}_m^{(N-1)}(x) = 0$, for $x = \pm A_m/2$, (2.28b)

v_m is a polynomial of degree $2N-1$ on $[-\frac{1}{2}A_m, 1-\frac{1}{2}A_m)$ and on $(\frac{1}{2}A_m-1, \frac{1}{2}A_m]$. (2.28c)

These conditions determine a unique v_m in $C^{N-1}(J_m)$. Now, put

$$v = \mathrm{Mix}(\{v_m\}, \{A_m\}, \{k_m\}) . \tag{2.29}$$

It is clear that v satisfies items *(i)* and *(ii)* of Definition 2.1. Moreover, with

$$X_n = 2\sum_{l=1}^{n}(k_l^{(1)} + k_l^{(2)})(1+l) , \tag{2.30}$$

we have, as $n \to \infty$,

$$\frac{1}{2X_n}\int_{-X_n}^{X_n} v(x)\,dx \to \theta<u_1> + (1-\theta)<u_2> , \tag{2.31a}$$

$$\frac{1}{2X_n}\int_{-X_n}^{X_n} \psi_v(x)\,dx \to \theta<\psi_{u_1}> + (1-\theta)<\psi_{u_2}> , \tag{2.31b}$$

and, hence, v satisfies item *(w)* of Definition 2.3 and is in $W^{\circ}(\tilde{\psi})$ with

$$[v]^{\circ} = a , \qquad [\psi_v]^{\circ} = \theta<\psi_{u_1}> + (1-\theta)<\psi_{u_2}> . \tag{2.32}$$

In view of (2.21), $\Psi(a) \le [\psi_v]^{\circ}$, and we have

$$\Psi(a) \le \theta<\psi_{u_1}> + (1-\theta)<\psi_{u_2}> \tag{2.33}$$

for *each* pair (u_1, u_2) of the functions in $W_1(\tilde{\psi})$ with $<u_1> = a_1$, $<u_2> = a_2$. The relation (2.23) follows forthwith from (2.21) and (2.33), and hence Ψ is convex on $\mathbb{R}$.

As Ψ is convex, is strictly less than ∞, and has a finite value at a_o, Ψ is real-valued on $\mathbb{R}$;

q.e.d.

Now, for each λ in $\mathbb{R}$ let

$$\Phi(\lambda) := \inf \{ [\psi_u] - \lambda < u > \mid u \in W(\tilde{\psi}) \}, \tag{2.34}$$

and note that, by Lemma 2.1,

$$\Phi(\lambda) = \inf \{ < \psi_u > - \lambda < u > \mid u \in W_1(\tilde{\psi}) \}. \tag{2.35}$$

When we interpret $\Psi(a)$ as the *mean Helmholtz free energy for equilibrium at average concentration a* , it is not inconsistent with the terminology of chemical thermodynamics to then refer to $\Phi(\lambda)$ as the *mean Gibbs free energy for equilibrium at potential*# λ.

I.e., for equilibrium at value λ of the chemical potential.

The convex conjugate Ψ^* of the convex function Ψ is, by definition,#

E.g., [1970].

$$\Psi^*(\lambda) := \sup \{ a\lambda - \Psi(a) \mid a \in \mathbb{R} \} . \tag{2.36}$$

Theorem 2.2. The Gibbs function $\Phi: \mathbb{R} \rightarrow [-\infty, \infty]$ defined in (2.34) is concave on $\mathbb{R}$; in fact

$$\Phi = -\Psi^{*}. \tag{2.37}$$

If $\Phi > -\infty$ on $\mathbb{R}$, then Ψ and Φ are continuous real-valued functions and

$$\Psi(a)/|a| \rightarrow \infty, \quad \text{as} \quad |a| \rightarrow \infty, \tag{2.38}$$

$$\Phi(\lambda)/|\lambda| \rightarrow -\infty, \quad \text{as} \quad |\lambda| \rightarrow \infty. \tag{2.39}$$

Proof. In view of (2.35) and (2.36),

$$\begin{aligned} -\Phi(\lambda) &= \sup \{ \lambda<u> - <\psi_u> \mid u \in W_1(\tilde{\psi}) \} \\ &= \sup_{a\in \mathbb{R}} \sup \{ \lambda a - <\psi_u> \mid u \in W_1(\tilde{\psi}),\ <u> = a \} \\ &= \sup \{ \lambda a - \Psi(a) \mid a \in \mathbb{R} \} = \Psi^{*}(\lambda), \end{aligned} \tag{2.40}$$

which proves (2.37) and the convexity of $-\Phi$ on $\mathbb{R}$, i.e., the concavity of Φ on $\mathbb{R}$.

Now, suppose $\Phi > -\infty$ on $\mathbb{R}$. Then, as Φ is concave, either $\Phi \equiv \infty$ or Φ is real-valued and continuous on $\mathbb{R}$. Since for each a,

$$\Phi(0) \leq \Psi(a) \leq \tilde{\psi}_0(a), \tag{2.41}$$

Φ *is* real-valued and continuous, and, by Theorem 2.1, Ψ is real-valued on $\mathbb{R}$. As

$$(-\Phi)^{*} = \Psi^{**} = \Psi, \tag{2.42}$$

(2.39) follows. As $\Psi^* = -\Phi$, and $-\Phi$ is real-valued and convex on $\mathbb{R}$, the same type of reasoning yields (2.38); q.e.d.

Remark. Our proofs that Ψ is convex and never $+\infty$, and the implication that Φ is concave are independent of our assumption that there is a point a_0 at which $\Psi(a_0) > -\infty$. To show that Ψ is real-valued for a particular class of materials, one may first show that for that class of materials Φ is real-valued and hence (2.41) yields not only $\Psi(a) < \infty$, but also $\Psi(a) > -\infty$ for all a. Moreover, (2.41), convexity of Ψ, and real-valuedness of Φ suffice for proof of (2.38) and (2.39). The function Φ is real-valued under very general conditions on $\tilde{\psi}$. Such a set of conditions is provided by the following lemma.

Lemma 2.3. Let $\tilde{\psi}$ be a continuous function from $\mathbb{R}^{N+1}$ to $\mathbb{R}$ obeying, for each triple $(w, \mathbf{s}, z)$ in $\mathbb{R} \times \mathbb{R}^{N-1} \times \mathbb{R}$,

$$c_1|w|^{\gamma_1} - c_2|\mathbf{s}|^{\gamma_2} + c_3|z|^{\gamma_3} + d \;\le\; \tilde{\psi}(w, \mathbf{s}, z), \tag{2.43}$$

where d, c_j, γ_i are constants and

$$1 \le \gamma_2 < \gamma_1, \quad \gamma_2 \le \gamma_3, \quad 1 < \gamma_3, \quad \text{and } c_j > 0 \text{ for } j = 1, 2, 3. \tag{2.44}$$

Then $\Phi(\lambda)$, defined by (2.34), is finite for each real number λ. In fact, there is then a real-valued function M_λ of λ which is bounded on each compact interval and is such that, for every $X \geq 1$ and every u in $C^{N-1}([-X,X])$ with $u^{(N-1)}$ absolutely continuous,

$$\frac{1}{2X}\int_{-X}^{X}[\,\tilde{\psi}(u,u',\ldots,u^{(N)}) - \lambda u\,]\,dx \;\geq\; \frac{1}{2X}\int_{-X}^{X}\frac{c_3}{2}|u^{(N)}|^{\gamma_3}\,dx - M_\lambda . \tag{2.45}$$

Proof. As $\Phi(\lambda) \leq \tilde{\psi}(0,\ldots,0)$, our goal is to show that $\Phi(\lambda)$ is not $-\infty$. Let I be a closed interval with length $|I|$ obeying $1 \leq |I| \leq 2$, and let p obey $1 \leq p < \infty$. According to the interpolation inequality for Sobolev spaces,[#] for each $\varepsilon > 0$ there is a

[#] E.g., [1975], p. 70.

positive constant $c(\varepsilon)$ such that

$$\int_I |u^{(j)}|^p dx \;\leq\; \varepsilon\int_I |u^{(N)}|^p dx + c(\varepsilon)\int_I |u|^p dx, \qquad j = 1,\ldots,N-1, \tag{2.46}$$

for every u in $C^N(I)$ with $u^{(N-1)}$ absolutely continuous. Hence,

$$\int_I |u^{(j)}|^{\gamma_2}dx \;\leq\; \varepsilon|I|^{1-\alpha}\left[\int_I |u^{(N)}|^{\gamma_3}\,dx\right]^{\alpha} + c(\varepsilon)\int_I |u|^{\gamma_2}dx \tag{2.47}$$

with $\alpha = \gamma_2/\gamma_3 \leq 1$, and this implies

$$\int_I |u^{(j)}|^{\gamma_2} dx \le 2\varepsilon \int_I |u^{(N)}|^{\gamma_3} dx + c(\varepsilon) \int_I |u|^{\gamma_2} dx + 2\varepsilon, \qquad j=1,\dots,N-1 . \tag{2.48}$$

Now, for $X \ge 1$ let u be a function in $C^{N-1}([-X, X])$ with $u^{(N-1)}$ absolutely continuous. Choose an l so that $2X/l = k$ is an integer. By applying (2.48) to the function u on each of the intervals $I = I_m = [-X+(m-2)l, \ -X+ml]$, $m=1,\dots,k$, and summing over m, one obtains, for $j=1, \dots, N-1$,

$$\frac{1}{2X} \int_{-X}^{X} |u^{(j)}|^{\gamma_2} dx \le \frac{\varepsilon}{X} \int_{-X}^{X} |u^{(N)}|^{\gamma_3} dx + \frac{c(\varepsilon)}{2X} \int_{-X}^{X} |u|^{\gamma_2} dx + 2\varepsilon . \tag{2.49}$$

If we put $\varepsilon = c_3/(4Nc_2)$, $\beta_1 = (N-1)c(\varepsilon)$, and $\beta_2 = (N-1)\varepsilon - d$, then (2.49) and (2.43) yield

$$\frac{1}{2X} \int_{-X}^{X} \bar{\psi}(u, u', \dots, u^{(N)}) \ge \frac{1}{2X} \int_{-X}^{X} \frac{c_3}{2} |u^{(N)}|^{\gamma_3} dx - \frac{1}{2X} \int_{-X}^{X} (\beta_1 |u|^{\gamma_2} - c_1 |u|^{\gamma_1})\, dx - \beta_2 . \tag{2.50}$$

Let

$$M_\lambda = \sup \{ \beta_1 t^{\gamma_2} - c_1 t^{\gamma_1} - \lambda t \mid t \in \mathbb{R} \} + \beta_2 , \tag{2.51}$$

and note that as $\gamma_1 > \gamma_2 \ge 1$, we have $M_\lambda < \infty$, and the relation (2.45) follows from (2.50). As (2.45) yields $\Phi(\lambda) \ge -M_\lambda$, the lemma is proven.

3. Equilibrium of Second-Order Materials

In this section we discuss a class of second-order materials for which $\tilde{\psi}$, in the equation

$$\psi = \tilde{\psi}(u, u', u'') , \tag{3.1}$$

is in $C^2(\mathbb{R}^3)$, is convex in its last variable, *i.e.*,

$$\partial^2 \tilde{\psi}(w,p,r)/\partial r^2 \geq 0 , \tag{3.2}$$

and satisfies

$$c_1|w|^{\gamma_1} - c_2|p|^{\gamma_2} + c_3|r|^{\gamma_3} + d \leq \tilde{\psi}(w,p,r) \leq f(w,p) + c_4|r|^{\gamma_3} , \tag{3.3}$$

where f is a continuous function, d, c_j, γ_i are constants, and

$$1 \leq \gamma_2 < \gamma_1 , \quad \gamma_2 \leq \gamma_3 , \quad 1 < \gamma_3, \quad \text{and } c_j > 0 \text{ for } j = 1,\dots,4. \tag{3.4}$$

This class of materials includes those for which (1.38) – (1.40) hold. Each material obeying (3.1) – (3.4) also obeys the hypotheses of Lemma 2.3 and hence the assumptions of Section 2. In particular, Theorem 2.1 and Lemmata 2.1 and 2.2 can be employed here. The results of Leizarowitz and Mizel [1989] described in Section 1 are also valid under the present assumption of (3.1) – (3.4).

We shall here present a method by which one can construct states u_a that solve the constrained minimization problem,

(P_a) Find $\Psi(a) = \inf \{ [\psi_u] \mid u \in W(\tilde{\psi}), \ < u > = a \}$, $\quad a \in \mathbb{R}$, using states u_λ that solve the unconstrained problem

$$(\mathrm{P}^\lambda) \qquad \text{Find} \quad \Phi(\lambda) = \inf\{\, [\psi_a] - \lambda u \;|\; u \in W(\tilde{\psi}) \,\}, \quad \lambda \in \mathbb{R}.$$

We shall observe that for certain values of a, namely those that are exposed points of the function Ψ, there are corresponding values of λ such that every state u_λ that solves# (P^λ)

We say that u "solves" (P^λ) or (P_a) if the infimum in that problem is attained at u.

also solves (P_a). However, in general there may be values of a for which states that solve (P_a) cannot be obtained in this manner. We shall show that, for each such value of a, (P_a) is solved by either a limit of a sequence $\{u_{\lambda_n}\}$ of states, with u_{λ_n} solving (P^{λ_n}), or by a mixture of two such limiting states. This will lead us to the following result (Theorem 3.1): For every a, there is a state u_a that solves (P_a) and that is either periodic or is a mixture of a pair of periodic states. We shall also observe (Theorem 3.2) that, for materials obeying relations of the form

$$\tilde{\psi}(w,p,r) \le h(w,r) - bg(p) \tag{3.5}$$

in which b is a positive constant and h and g are non-negative continuous functions with $g(p) = 0$ only when $p = 0$, for each compact interval I there is a critical value

$b_0 = b_0(h, g, I)$ of b such that if b exceeds b_0 and a is in I, (P_a) is not solved by states for which u_a is constant on $\mathbb{R}$. Materials obeying the relations (1.38) – (1.40) obey not only (3.1) – (3.4), but also (3.5).

The concepts of support point and exposed point, mentioned in Section 1,# are here

Cf. (1.13) and (1.14).

employed in a form that is meaningful for functions not necessarily differentiable everywhere. We say that a point a in $\mathbb{R}$ is a *support point* for a real-valued function g on $\mathbb{R}$ if there is a λ in $\mathbb{R}$ such that,

$$g(y) \geq g(a) + \lambda(y - a), \qquad \text{for all } y \in \mathbb{R}; \tag{3.6}$$

a is an *exposed point* if, in addition, there is a λ in $\mathbb{R}$ for which,

$$g(y) > g(a) + \lambda(y - a), \qquad \text{when } y \neq a. \tag{3.7}$$

The set $\partial g(a)$ of all λ in $\mathbb{R}$ for which (3.6) holds is the *subdifferential* of g at a.

As Ψ is convex, when Ψ is real-valued $\partial\Psi(a)$ is a nonempty bounded set for each a in $\mathbb{R}$,# and Ψ is differentiable at a if and only if $\partial\Psi$ is a singleton, in which case

Vid., e.g., [1970].

$\partial\Psi(a) = \{ \Psi'(a) \}$. If Ψ is *not* differentiable at a, then $\partial\Psi(a)$ is a compact interval $[\lambda_l(a), \lambda_r(a)]$ with $\lambda_l < \lambda_r$, and in that case (3.7) must hold for each λ in $(\lambda_l(a), \lambda_r(a))$. Thus, every point at which Ψ is not differentiable is an exposed point for Ψ.

Concerning exposed points for Ψ, we have the following lemma, which holds for general materials obeying the hypotheses of Section 2, once it is granted that Φ, and hence Ψ, is real-valued.

Lemma 3.1. Let a be an exposed point for Ψ, and let λ obey (3.7) with $g = \Psi$. Then every function u_λ in $W(\tilde{\psi})$ at which the infimum in (P^λ) is attained, i.e., for which $[\psi_{u_\lambda}] - \lambda\langle u_\lambda\rangle = \Phi(\lambda)$, is one at which the infimum in (P_a) is attained, i.e., is in $U(a)$ and has $[\psi_{u_\lambda}] = \Psi(a)$.

Proof. If u_λ minimizes the right side of (2.34), we have, by (2.37),

$$[\psi_{u_\lambda}] - \lambda\langle u_\lambda\rangle = \Phi(\lambda) = \inf\{ \Psi(y) - \lambda y \mid y \in \mathbb{R} \} . \tag{3.8}$$

Our assumptions about a and λ assert that

$$\Psi(y) - \lambda y > \Psi(a) - \lambda a , \qquad \text{for } y \neq a, \tag{3.9}$$

and hence the infimum in (3.8) is attained when, and only when, $y = a$. Thus,

$$\Psi(a) - \lambda a = [\psi_{u_\lambda}] - \lambda\langle u_\lambda\rangle \geq \Psi(\langle u_\lambda\rangle) - \lambda\langle u_\lambda\rangle, \tag{3.10}$$

and on comparing this with (3.8) we deduce first that $\langle u_\lambda\rangle = a$ and then that $\Psi(a) = [\psi_{u_\lambda}]$; q.e.d.

For materials obeying (3.1) – (3.4), the Lemma just proven and the results of Leizarowitz and Mizel [1989] imply that *when a is an exposed point for Ψ there is a periodic state u_a that solves the problem* (P_a).

We consider now points a which are not exposed points for Ψ. As Ψ is convex, for each such point there are numbers $a_1 = a_1(a) < a_2 = a_2(a)$ and $\lambda_0 = \lambda_0(a)$ for which

$$\Psi(y) = \lambda_0(y - a) + \Psi(a), \qquad \text{for } y \text{ in } [a_1, a_2]. \tag{3.11}$$

By (2.38), the interval $[a_1, a_2]$ is bounded; we take it to be the maximal interval containing a on which (3.11) holds, i.e., on which Ψ is affine. Clearly, the infimum in (3.8) with $\lambda = \lambda_0(a)$ is attained if and only if y is in $[a_1, a_2]$. Therefore, if v is a solution of (P^{λ_0}) then, as in the proof of the previous lemma, it follows that a_0, the average of v, is in $[a_1, a_2]$ and consequently v solves (P_{a_0}). Thus, given $\lambda_0(a)$ for an a which is not exposed, we can find a state v that solves a constrained problem (P_{a_0}) with a_0 in $[a_1, a_2]$, *but a_0 need not equal the original a.*

In our treatment of the problem (P_a) for values of a that are not exposed points for Ψ, we confine our attention to second-order materials obeying (3.2) – (3.4). For our next lemma we employ the following result, recently obtained by Leizarowitz [1990] using a refinement of arguments given in [1989]: *Let I be a bounded interval. As* λ *varies over I, for each* λ *a periodic function* u_λ *that solves* (P^λ) *can be selected so that* (i) *the set* $\{ T_\lambda \mid \lambda \in I \}$, with T_λ *the minimal period of* u_λ, *is bounded, and* (ii) *the functions* u_λ *and* u'_λ, $\lambda \in I$, *are uniformly bounded.*

Lemma 3.2. Assume (3.1) – (3.4), and suppose that $[a_1, a_2]$ is a maximal interval on which Ψ is affine. Then there are periodic functions u_{a_1} and u_{a_2} in $W_1(\tilde{\psi})$ that solve the problems (P_{a_1}) and (P_{a_2}).

Proof. We consider a_2. The proof for a_1 is analogous. If Ψ is not differentiable at a_2, then a_2 is an exposed point for Ψ and the required result follows from Lemma 3.1. Therefore, we suppose that Ψ is differentiable at a_2 and note that Ψ' is then continuous at a_2. We claim that, for every $\varepsilon > 0$, the interval $J_\varepsilon = (a_2, a_2 + \varepsilon)$ contains an exposed point for Ψ. As this is obvious if there is a point in J_ε at which Ψ is not differentiable, we suppose for the moment that there is an $\varepsilon > 0$ such that Ψ' is continuous on J_ε. Then, $\Psi'(J_\varepsilon)$ is an interval and this interval is not degenerate, because, by the maximality of $[a_1, a_2]$, $\Psi'(a) > \Psi'(a_2)$ for each a in J_ε, and Ψ' is continuous at a_2. As the maximal nonsingleton subsets of J_ε on which Ψ' is constant are disjoint intervals, they form a countable set; if Q is their union, $\Psi'(Q)$ cannot cover the interval $\Psi'(J_\varepsilon)$. Thus, $J_\varepsilon \setminus (Q)$ is not empty. If a is in $J_\varepsilon \setminus (Q)$ then $\Psi'(a-\delta) < \Psi'(a) < \Psi'(a+\delta)$ for every $\delta > 0$, and hence a is an exposed point for Ψ.

In view of the above, there is a strictly decreasing sequence $\{a^{(n)}\}$ of exposed points for Ψ with $a^{(n)} \to a_2$. For each n, let $\lambda^{(n)}$ be a number in $\partial\Psi(a^{(n)})$ such that (3.7) holds with $g = \Psi$, $a = a^{(n)}$, $\lambda = \lambda^{(n)}$. Then $\Psi'(a_2) < \lambda^{(n)} \leq \Psi'(a^{(n)}+)$, and hence $\lambda^{(n)} \to \lambda_0 = \Psi'(a_2)$. As Φ is finite-valued and concave, Φ is continuous and $\Phi(\lambda^{(n)}) \to \Phi(\lambda_0)$. If $u_{(n)}$ minimizes the right side of (2.34) with $\lambda = \lambda^{(n)}$, by Lemma 3.1, $<u_{(n)}> = a^{(n)}$ and $\Phi(\lambda^{(n)}) = [\psi_{u(n)}] - \lambda^{(n)}a^{(n)} = \Psi(a^{(n)}) - \lambda^{(n)}a^{(n)}$. Thus, by the continuity of Φ and Ψ:

$$\Phi(\lambda_0) = \Psi(a_2) - \lambda_0 a_2 . \tag{3.12}$$

Now, in view of the theory presented in [1989] and the previously mentioned result of Leizarowitz [1990], we can choose the functions $u_{(n)}$ that solve $(P^{\lambda^{(n)}})$ so that they are periodic and their minimal periods $T^{(n)}$ are bounded and, moreover, so that the functions $u_{(n)}$ and $u'_{(n)}$ are uniformly bounded on IR and each function $u_{(n)}$ obeys (1.41). In view of the coercivity relation (2.45), which is implied by (3.3), we conclude that the functions $u_{(n)}$ are also uniformly bounded in the space $W^{2,\gamma_3}_{\text{loc}}$ formed from functions v on IR with v and v′ absolutely continuous and with $|v''|^{\gamma_3}$ locally integrable. By extraction of a subsequence, we obtain a new sequence of periodic functions $u_{(n)}$ whose minimal periods $T^{(n)}$ converge while $\{u_{(n)}\}$ converges weakly in $W^{2,\gamma_3}_{\text{loc}}$ and uniformly in $C^1(\mathbb{R})$ to a periodic function u_0 in $W^{2,\gamma_3}_{\text{loc}}$ with period $T_0 = \lim_{n\to\infty} T^{(n)}$. Then

$$<u_0> = \lim_{n\to\infty} <u_{(n)}> = a_2, \tag{3.13}$$

and, by Tonelli's theorem on lower semicontinuity,

$$[\psi_{u_0}] \le \lim_{n\to\infty} \inf [\psi_{u_{(n)}}]. \tag{3.14}$$

As $[\psi_{u_{(n)}}] = \Psi(a^{(n)})$ and $\lim_{n\to\infty} \Psi(a^{(n)}) = \Psi(a_2)$, (3.14) yields

$$[\psi_{u_0}] \le \Psi(a_2). \tag{3.15}$$

Hence u_0 is a periodic function that solves problem (P_{a_2}), which completes our proof. It is not difficult to see that u_0 describes a state of minimal free energy in the sense of (1.41) and, by (3.11), is a state at which the infimum (2.34) is attained with $\lambda = \lambda_0 = \Psi'(a_2)$, i.e., $\Phi(\lambda_0) = <\psi_{u_0}> - \lambda_0 <u_0>$.

Definition 3.1. We say that a continuous real-valued function u on $\mathbb{R}$ is an *asymptotically twice-periodic mixture* of two periodic, continuous functions $u_{(1)}$, $u_{(2)}$ on $\mathbb{R}$ if u is uniformly bounded and there is a sequence $\{K_i\}$ of disjoint intervals with $|K_i| \to \infty$ such that:

(i) On K_i, $u = u_{(1)}$ if i is odd and $u = u_{(2)}$ if i is even.

(ii) $\lim_{X\to\infty} \frac{1}{2X} \sum_{i=1}^{\infty} |K_i \cap I| = 1$, with $I = [-X, X]$.

(iii) With I as in (ii), $\dfrac{\sum_{i \text{ odd}} |K_i \cap I|}{\sum_{i \text{ even}} |K_i \cap I|}$ converges to a positive number τ as $X \to \infty$.

The number $\theta = \tau/(1+\tau)$ is called the *fraction of the mixture containing* $u_{(1)}$.

Lemma 3.3. Assume (3.1) – (3.4). Let $[a_1, a_2]$ be as in Lemma 3.2, and let u_{a_1} and u_{a_2} be periodic functions in $W_1(\tilde{\psi})$ that solve (P_{a_1}) and (P_{a_2}). If a is interior to $[a_1, a_2]$, i.e., if $a = \theta a_1 + (1-\theta)a_2$ with $0 < \theta < 1$, then the problem (P_a) is solved by an asympotically twice periodic mixture u^* of u_{a_1} and u_{a_2} with θ the fraction of the mixture containing u_{a_1}.

Proof. Let T_j be a (not necessarily minimal) period of u_{a_j}, $j = 1, 2$. If u_j is constant put $T_j = 1$. Let $\{\nu_n\}$ be an unbounded sequence of positive numbers for which as $n \to \infty$

$$\frac{\nu_{2n-1}T_1}{\nu_{2n}T_2} \to \frac{\theta}{1-\theta} \quad \text{and} \quad \frac{\nu_{2n}}{\sum_{m=0}^{n-1} \nu_{2n}} \to 0. \tag{3.16}$$

Let $X_m = \nu_m T_1$ if m is odd and $X_m = \nu_m T_2$ if m is even, and put $J_m = [-X_m-1,\ X_m+1]$. Define v_m on the interval J_m by the equations (2.15a)–(2.15c) of the proof of Lemma 2.1 with $N = 2$ and $u = u_{a_1}$ for m odd and $u = u_{a_2}$ for m even. Finally, put

$$u^* = \mathrm{Mix}\left(\{\mathrm{v}_m\}, \{A_m\}, \{k_m\}\right) \tag{3.17}$$

with

$$A_m = 2(X_m-1), \quad k_m \equiv 1. \tag{3.18}$$

Then u^* is in $W_1(\tilde{\psi})$,

$$<u^*> = \theta<u_{a_1}> + (1-\theta)<u_{a_2}> = \theta a_1 + (1\text{-}\theta)a_2 = a, \tag{3.19}$$

and

$$<\psi_{u^*}> = \theta<\psi_{a_1}> + (1-\theta)<\psi_{a_2}> = \theta\Psi(a_1) + (1\text{-}\theta)\Psi(a_2). \tag{3.20}$$

As Ψ is affine on $[a_1,\ a_2]$, (3.20) yields

$$<\psi_{u^*}> = \Psi(a), \tag{3.21}$$

which completes the proof.

Let g be a real-valued convex function on $\mathbb{R}$. A number a is called an *extreme point* for g if it is not interior to an interval on which g is affine, i.e., if there is no open interval (a_1, a_2) with $a \in (a_1, a_2)$ and no λ in $\mathbb{R}$, for which $g(y) = g(a_1) + \lambda(y - a_1)$ for all y in $[a_1, a_2]$.

Lemmata 3.1 – 3.3 and remarks made in their proofs yield the following two theorems.

Theorem 3.1. If the material is of order 2 and $\tilde{\psi}$ obeys (3.2) – (3.4), then for each a in $\mathbb{R}$ the convex function Ψ is finite-valued and there is an equilibrium state u_a with $\langle u_a \rangle = a$. If a is an extreme point for Ψ, then u_a can be chosen to be a periodic function that describes a state of minimal free energy in the sense of (1.41). On the other hand, if a is not an extreme point for Ψ, and if u_{a_1} and u_{a_2} are two periodic equilibrium states with $\langle u_{a_1} \rangle = a_1$ and $\langle u_{a_2} \rangle = a_2$, where a_1 and a_2 are the end points of the maximal interval containing a on which Ψ is affine, then the state u_a can be chosen to be an asymptotically twice-periodic mixture of the states u_{a_1} and u_{a_2}.

The following theorem applies to a class of materials of order $N \geq 2$ that includes not only those of order 2 obeying (1.38) and (1.39), or their generalization (3.5), but also those of order $N \geq 2$ for which $\tilde{\psi}$ is a continuous function on $\mathbb{R}^{(N-1)}$ obeying, for each triple $(w, \mathbf{s}, z)$ in $\mathbb{R} \times \mathbb{R}^{N-1} \times \mathbb{R}$,

$$\tilde{\psi}(w, \mathbf{s}, z) \leq c(|w| + |z|)^{\nu_1} - b|\mathbf{s}|^{\nu_2} + \eta, \tag{3.22}$$

where $\nu_1, \nu_2, b, c,$ and η are positive constants, and, as in (2.43), $w = u$, $\mathbf{s} = (u', ..., u^{(N-1)})$, and $z = u^{(N)}$.

Theorem 3.2. Suppose $\tilde{\psi}$ is a continuous function on $\mathbb{R}^{N+1}$, $N \geq 2$, obeying

$$\tilde{\psi}(u, u', u'', ..., u^{(N)}) \;\leq\; h(u, u', ..., u^{(N)}) - bg(u', ..., u^{(N-1)}) \tag{3.23}$$

with b a positive constant and with h and g continuous non-negative functions on $\mathbb{R}^{N+1}$ and $\mathbb{R}^{N-1}$, respectively. Assume that g is positive definite in the sense that $g(s_1, ..., s_{N-1}) = 0$ if $s_i = 0$ for $i = 1, ..., N-1$, and $g(s_1, ..., s_{N-1}) > 0$ otherwise. Define Ψ and $\tilde{\psi}_0$ by (1.10) and (1.12). For each compact interval I in $\mathbb{R}$, there is a positive number $b_0 = b_0(h, g, I)$ such that if $b > b_0$, then for each a in I,

$$\Psi(a) < \operatorname{conv} \tilde{\psi}_0(a), \tag{3.24}$$

and hence there is no spatially uniform (*i.e.*, almost everywhere constant) equilibrium state with average value a.

Proof. Let $v = \sin x$, and put

$$K = \sup \{ \; h(v(x)+a,\, v'(x),\ldots,v^{(N)}(x)) \mid x \in \mathbb{R},\, a \in I \;\}, \tag{3.25a}$$

$$\sigma = \min \{ \; g(v'(x),\ldots,v^{(N-1)}(x)) \mid x \in \mathbb{R} \;\}. \tag{3.25b}$$

As the set $\{ \; (v'(x),\ldots,v^{(N-1)}(x)) \mid x \in \mathbb{R} \;\}$ is compact in $\mathbb{R}^{N-1}$ and does not contain $(0,\ldots,0)$, the number σ is positive. By (3.23),

$$< \psi_{v+a} > \;=\; \frac{1}{2\pi}\int_0^{2\pi} \psi_{v+a}(x)dx \;\le\; K - b\sigma\;. \tag{3.26}$$

Now, as $\tilde{\psi}$ is continuous, for each compact interval I, the number,

$$\mu = \min \{ \; \mathrm{conv}\, \tilde{\psi}_0(a) \mid a \in I \;\}, \tag{3.27}$$

is finite. As $\sigma > 0$, there is a number b_0 such that for all $b > b_0$

$$K - b\sigma < \mu \tag{3.28}$$

and, in view of (1.10) and (3.26),

$$\Psi(a) \le \;<\psi_{v+a}>\; < \; \mathrm{conv}\, \tilde{\psi}_0(a) \tag{3.29}$$

for each a in I; q.e.d.

Of course, the hypothesis of Theorem 3.2 does not insure that the infimum in (1.10) is attained or even that $\Psi(a)$ in (3.24) is $> -\infty$.

Arguments we have given in this section, particularly in the proof of Lemma 3.1, and the paragraph containing equation (3.11), justify the following general remark about materials with $N \geq 1$.

Remark. Consider a material of order one or higher, and suppose that $\tilde{\psi}$ is such that for each λ in $\mathbb{R}$ there is a state that solves (P^λ), i.e., that for each λ the infimum $\Phi(\lambda)$ of $\{ [\psi_u - \lambda u] \mid u \in W(\tilde{\psi}) \}$ is finite and is attained at a function in $W(\tilde{\psi})$.

(*i*) If $a = \langle u_\lambda \rangle$, where u_λ solves (P^λ), then not only is u_λ an equilibrium state with average concentration a, but

$$\Psi(a) = \Phi(\lambda) + \lambda a. \tag{3.30}$$

(*ii*) Whenever a is an exposed point for the finite-valued convex function Ψ, equilibrium states with average concentration a may be found as follows: Let λ be one of the numbers for which

$$\Psi(y) > \Psi(a) + \lambda(y-a) \quad \text{when } y \neq a; \tag{3.31}$$

each state u_λ that solves (P^λ) is an equilibrium state with $\langle u_\lambda \rangle = a$; if Ψ is differentiable at the exposed point a, then λ is unique and $\lambda = \Psi'(a)$.

4. Remarks on Homogenization

In the theory presented in this paper we have regarded bodies of infinite extent as limits of bodies of finite extent. Indeed, we have defined averages of functions on $\mathbb{R}$ to be the limits of averages over intervals of finite length; e.g., if u on $\mathbb{R}$ is such that $\langle u \rangle$ in (1.1) exists, then

$$\langle u \rangle = \lim_{X \to \infty} \langle u \rangle_X , \tag{4.1}$$

where

$$\langle u \rangle_X := \frac{1}{2X} \int_{-X}^{X} u \, dx \tag{4.2}$$

is the average value of the concentration for a body of length $2X$ whose state u is obtained by restricting $u\colon \mathbb{R} \to \mathbb{R}$ to the interval $I_X = [-X, X]$. Here, in a trivial sense, the state u of an infinite body is the pointwise limit, as $X \to \infty$, of the states of finite bodies.

There is, however, a way to start with one-parameter families of functions $u|_{I_X}$ and build up a theory appropriate to the limit of large X in which $\langle u \rangle$ and $[\psi_u]$ of the present theory may be interpreted as quantities defined for states of a limiting body of finite length. In this procedure, as X increases the x-axis is rescaled by the transformation

$$x \mapsto y = \varepsilon x , \qquad \varepsilon = 1/X , \tag{4.3}$$

and thus at each stage one deals with function u_ε defined on the interval $I_1 = [-1, 1]$ by

$$u_\varepsilon(y) = u(x) = u(y/\varepsilon)\,. \tag{4.4}$$

An expected feature of this procedure of homogenization is that as $X \to \infty$ the limit of u_ε will be not a function, but a Young measure. We briefly examine the procedure below.

Let $\tilde{\psi}$ be the Helmholtz free-energy function for a material of the order $N \geq 1$, and let $W(\tilde{\psi})$ be defined as in the first paragraph of Section 2. For each u in $W(\tilde{\psi})$, the derivatives of the function u_ε on I_1 obtained from the restriction of u to I_X as in (4.5) obey

$$u'(y/\varepsilon) = \varepsilon u_\varepsilon'(y), \qquad u''(y/\varepsilon) = \varepsilon^2 u_\varepsilon''(y)\,, \qquad \text{etc.} \tag{4.5}$$

We continue to write $<\cdot>_X$ for the average value of a function on I_X. Clearly,

$$<u>_X := <u_\varepsilon>_1\,. \tag{4.6}$$

With the notation,

$$\psi_{\mathrm{v}}^{\varepsilon}(y) = \tilde{\psi}(\mathrm{v}(y), \varepsilon \mathrm{v}'(y), \varepsilon^2 \mathrm{v}''(y), \ldots, \varepsilon^N \mathrm{v}^{(N)}(y))\,, \tag{4.7}$$

we have, by (1.4), (4.4), and (4.5),

$$<\psi_u>_X := \frac{1}{2X}\int_{-X}^{X} \tilde{\psi}(u(x), u'(x), u''(x), \ldots, u^{(N)}(x))dx$$

$$= \frac{1}{2}\int_{-1}^{1} \psi^{\varepsilon}_{u_\varepsilon}(y)\,dy = <\psi^{\varepsilon}_{u_\varepsilon}>_1 . \tag{4.8}$$

As u is in $W(\tilde{\psi})$, (4.6) and (4.8) yield,

$$\lim_{\varepsilon\to 0} <u_\varepsilon>_1 = <u>, \tag{4.9}$$

$$\lim_{\varepsilon\to 0} \inf <\psi^{\varepsilon}_{u_\varepsilon}>_1 = [\,\psi_u\,]. \tag{4.10}$$

As each u in $W(\tilde{\psi})$ is in $L^\infty(\mathbb{R})$, the family $\{u_\varepsilon\}$ is a bounded subset of $L^\infty(I_1)$, and it follows that each sequence $\{\varepsilon_m\}$ with $\varepsilon_m \to 0$ has subsequence $\{\varepsilon_{m'}\}$ for which, in the sense of weak convergence of measures,

$$u_{\varepsilon_{m'}} \overset{*}{\to} \nu , \tag{4.11}$$

where $\nu = \nu(y;\ d\lambda)$ is a *Young measure*. That is, for each Borel set E in $\mathbb{R}$, the function $y \mapsto \nu(y; E)$ is a Borel measurable function, while for almost every y in I_1, $E \mapsto \nu(y; E)$ is a probability measure on $\mathbb{R}$. Furthermore, given the subsequence $\{u_{\varepsilon_{m'}}\}$ for which (4.11) holds, by an elaboration of the method of Lemma 2.1 one can construct a state v in S that obeys (2.10) *and* is such that for a certain Young measure γ: (i) the analogue of (4.11) holds for *every* sequence $\{\varepsilon_i\}$ converging to zero, *i.e.*, as $\varepsilon \to 0$,

$$v_\varepsilon \xrightarrow{*} \gamma, \tag{4.12}$$

and (ii) γ determines a Borel probability measure μ that is independent of y, namely,

$$\gamma(y,E) = \mu(E) \quad \text{for all Borel sets } E, \text{ for almost all } y \text{ in } I_1 . \tag{4.13}$$

Consequently, the first moment of the probability measure μ gives the average value of u:

$$\int_{-\infty}^{\infty} \alpha \, d\mu(\alpha) = \langle u \rangle . \tag{4.14}$$

States that correspond to such *fiber-constant* Young measures can be regarded as possessing a generalized type of periodicity.

Definition 4.1. A function u in S is called *pseudoperiodic* if there is a Young measure γ on I_1 that obeys (4.13) and is related to the functions $\{u_\varepsilon\}$ by (4.12).

Remarks. (i) It is not difficult to verify that if a continuous function u describes a periodic state or an asymptotically twice-periodic mixture in the sense of Definition 3.1, then u is pseudoperioidic.

(ii) It can be shown that essentially bounded functions u on $\mathbb{R}$ which are almost periodic in the sense of Besicovitch are also pseudoperiodic. The connection between these generalized notions of periodicity will be further developed elsewhere.

The construction mentioned above ensures that for each u in $W(\tilde{\psi})$ there is a corresponding pseudoperiodic state $\tilde{u}$ in $W(\tilde{\psi})$ satisfying the conditions

$$<\tilde{u}> = <u>, \qquad <\psi_{\tilde{u}}> = [\psi_u]. \tag{4.15}$$

By using the preceding observations, one can obtain an existence result for functions solving the unconstrained problem (P^λ) for materials of arbitrary order $N \geq 2$. That existence result, together with the theory of Section 3, leads to the following theorem for materials obeying the natural extension to higher-order materials of the hypotheses (3.1) – (3.4).

Theorem 4.1. Suppose that for a material of order $N \geq 2$ the function $\tilde{\psi}$ is in $C^2(\mathbb{R}^N)$ and obeys, for each triple $(w, \mathbf{s}, z)$ in $\mathbb{R} \times \mathbb{R}^{N-1} \times \mathbb{R}$,

$$\partial^2 \tilde{\psi}(w, \mathbf{s}, z)/\partial z^2 \geq 0 \tag{4.16}$$

and

$$c_1|w|^{\gamma_1} - c_2|\mathbf{s}|^{\gamma_2} + c_3|z|^{\gamma_3} + d \le \tilde{\psi}(w,\mathbf{s},z) \le f(w,\mathbf{s}) + c_4|z|^{\gamma_3}, \tag{4.17}$$

with f continuous, d, c_j, γ_j constant, and

$$1 \le \gamma_2 < \gamma_1, \quad \gamma_2 \le \gamma_3, \quad 1 < \gamma_3, \quad \text{and } c_j > 0 \text{ for } j = 1,\dots,4. \tag{4.18}$$

Then not only is Ψ a real-valued convex function in accord with Theorem 2.2 and Lemma 2.3, but for each a in $\mathbb{R}$ there is a pseudoperiodic equilibrium state u_a in $W_1(\tilde{\psi})$ with $\langle u_a \rangle = a$.

Proofs and applications of the above observations will be presented elsewhere.

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We here present a theory of thermodynamical equilibrium for materials for which the free-energy density $\psi(x)$ depends not only on the concentration (or mass density) $u(x)$ and its gradient $u'(x)$, but also on $u''(x)$, the second gradient of u. We show that a broad class of such materials can exhibit equilibrium states that are periodic in a nontrivial way. It is possible that the theory of such second-order materials may supply insight into periodic layering phenomena observed in various types of mixtures, such as concentrated soap solutions and metallic alloys, but in this paper we do not refer to applications. Instead, we examine the mathematical implications of the theory.

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