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CONTINUUM THERMODYNAMICS WITH SURFACES:
RESTRICTIONS ON CONSTITUTIVE EQUATIONS

BY

GEORGE M. C. FISHER (*Bell Telephone Laboratories, Holmdel, New Jersey*)

AND

MARSHALL J. LEITMAN (*Case-Western Reserve University*)

Abstract. In an earlier paper we deduced, using measure theoretic concepts, forms for the first and second laws of thermodynamics on surfaces which are distinguished by area-continuous and time-dependent energy and entropy. In that paper we avoided making constitutive assumptions since we sought expressions for the physical laws which were, indeed, independent of particular material assumptions.

In this paper we show how one can proceed to make surface constitutive assumptions for a rigid heat conductor and, subsequently, use our forms of the first and second laws to obtain appropriate restrictions. In addition we show that admitting a term to account for "radiative" heat supply to the surface from outside the body leads naturally to the concept of surface temperature and also allows a much broader class of constitutive assumptions compatible with thermodynamics. As in the previous paper we shall, for simplicity, omit considerations of mechanical and electromagnetic effects as well as surface diffusion and line and point energy concepts. Some of these will be included at a later stage, but the prime concern here is to present a method for obtaining restrictions on surface constitutive assumptions.

Introduction. The concept of energy confined to some interface or surface layer has proven to be a convenient idealization in a great number of problems of scientific interest. Classical treatments, however, tend to make the surface quantities nothing more than two-dimensional analogues of the three-dimensional materials which the surface separates. This sometimes yields valuable results; however, it is important to realize that, more often than not, the microscopic regions which such surfaces represent are quite different in physical character from the surrounding material. For example, one might think of the interface between two dissimilar material phases. To model such a situation as a mathematical surface separating two well-behaved materials certainly assigns to the surface most of the physical properties of the phase transition. Indeed, this is the basic utility of the concept of such singular surfaces.

Since we are basically concerned in this work with energetic considerations of problems wherein the surface idealization might be a reasonable artifact, we take the first and second

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laws of thermodynamics as our basic physical laws. We adopt the view that the starting point for a critical and constructive reexamination of the field of surface concepts in continuum physics should be nonequilibrium surface thermodynamics.

We believe that one of the greatest sources of confusion in this subject has been the undue complication which workers impose by their failure to distinguish clearly between the consequences of the fundamental laws and those consequences which result from specialized constitutive assumptions applicable to particular problems. We feel that a careful distinction should be made in this respect. One must fully appreciate the formulation and implications of the basic laws governing surface phenomena, especially since the selection of the most suitable surface constitutive assumptions may be the weakest link in particular problems. Hence, in our first paper [9] on this subject we investigated the thermodynamic problem devoid of particular constitutive assumptions. In that paper we considered gross forms of the first and second laws in conjunction with the basic assumption that the total energy and entropy of any part of a body intersecting the singular surface is composed of a contribution from the surface in addition to the usual volumetric part. By developing sufficient geometric structure (essentially Boolean algebras of sets both on and off the surface) and imposing adequate continuity constraints, we were able to use some standard, but powerful, results of classical measure theory. Through this vehicle and the analogues to classical "pillbox" type arguments we deduced integral and local forms of the basic laws. For parts of the body not intersecting the surface the results are of course those obtained by Gurtin and Williams [8]. Up to this point we have neither considered constitutive assumptions for the surface nor for the surrounding materials. Thus we have established simple forms of the basic laws which should apply to materials with a broad range of physical response characteristics.

From an engineering point of view there is the obvious interest in solving practical boundary-value problems involving material behavior where time-dependent surface energy concepts are important. This is, of course, an ambitious undertaking in view of the complexities encountered in even the relatively simple problems where classical linear elasticity is an adequate description of material behavior. To attempt, however, to solve any particular problem necessitates a definite statement of constitutive assumptions which describe how a material will respond in a given experiment to the physical conditions it encounters. In selecting the relevant set of independent variables for our response functions we must appeal to the vast store of information obtained by chemists and physicists working under controlled experimental conditions. We are faced then with the problem of extrapolating to considerably more complex and certainly less ideal conditions. Some rational procedure is needed for considering our response functions with the assumed list of independent variables and subsequently deducing a reduced set of constitutive relations which are compatible with the laws of thermodynamics. Extensions of the now classical techniques of Coleman and Noll [2] do, in fact, yield the required restrictions on the surface response functions. In the present paper we demonstrate how such methods may be applied. Our prime concern here is to demonstrate, in as simple a physical context as possible, the techniques for obtaining the restrictions on surface constitutive assumptions.

In Sec. I we present that formulation of the first and second laws of thermodynamics which we feel is relevant to the discussion of surface phenomena. Most of the detailed mathematical structure is omitted here. However, we must bear in mind that justification of these results rests upon rigorous development of the fundamental laws. The analysis

presented in our earlier paper and that of Gurtin and Williams is easily modified to include the present context [9], [8]. We admit no internal radiation, which enables us easily to introduce a radiative source of heat r to the surface from the exterior of the body. As a result there exists, as a reciprocal Radon–Nikodym derivative, a surface temperature θ which plays a central role in the study of surface constitutive relations. The following extended local forms of the first two laws for the surface are obtained:¹

$$\dot{\epsilon} = [q] + r, \quad (\text{i})$$

$$\dot{\eta} \geq [q/\phi] + r/\theta, \quad (\text{ii})$$

where $\dot{\epsilon}$ is the time rate of change of surface energy density, q is the scalar heat flux, $\dot{\eta}$ is the time rate of change of the surface entropy density, and ϕ is the bulk conductive temperature which is defined off the surface and which may have different limiting values on opposite sides of the surface. It should be noted that the assumption of equal temperatures is quite strong in the present context. This point seems to emphasize our belief in the importance of clearly separating implications of the physical laws from the consequences of specialized material assumptions.

We show in Sec. II that Eqs. (i) and (ii), in conjunction with the modern techniques used to obtain constitutive restrictions from the laws of thermodynamics, suffice to give the following type of information. Let us assume, for example, for the stationary surface under consideration that q_+ , q_- , ϵ , and η are given by response functions which depend on ϕ_+ , ϕ_- , the limits of the gradients $(\text{grad } \phi)_+$, $(\text{grad } \phi)_-$, and the surface temperature θ .² With this set of assumptions we can show that necessary and sufficient conditions that Eqs. (i) and (ii) be satisfied are given by the following three statements:

(1) The surface energy ϵ , the surface entropy η , and consequently the surface free energy $\psi \equiv \epsilon - \theta\eta$ depend on *only* the surface temperature θ .

(2) The surface entropy is related to the surface free energy through

$$\eta = -d\psi/d\theta. \quad (\text{iii})$$

(3) The “heat conduction inequality” takes the following form:

$$[q/\phi] \leq \frac{1}{\theta} [q]. \quad (\text{iv})$$

This is only a simple illustrative example but serves to give an idea of the type of results we discuss in this paper.

Sec. III presents a brief discussion of some implications of the heat conduction inequality. In particular the consequences of a reasonable class of constitutive assumptions on q_+ , q_- are explored and the appropriate linearization obtained.

The reader interested only in the methods we describe for obtaining restrictions on constitutive assumptions may proceed directly to Secs. II and III, which are reasonably self-contained.

IV. CONSTITUTIVE THERMODYNAMICS WITH SURFACES. In this section we modify the results of our earlier analysis to include external surface radiative transfer. We omit virtually all the detailed

¹ We shall use the bracket notation $[f]$ to denote the “jump” in f across the surface.

² The notation f_+ or f_- denotes the limits of f from opposite sides of the surface.

mathematical arguments used to establish these results since they follow by simple extension of our earlier work and that of Gurtin and Williams.

We fix our attention upon a *body* \mathcal{B} which is a fixed region in three-dimensional Euclidean point space. This body contains a distinguished surface \mathcal{S} , called the *singular surface*, whose detailed thermodynamic characterization is our primary goal. By a *part* \mathcal{P} of \mathcal{B} we mean a sub-region of \mathcal{B} whose boundary $\partial\mathcal{P}$ may be regarded as composed of surfaces. Since we assume the body \mathcal{B} to be rigid and immobile, a material point in \mathcal{B} may be identified with its place \mathbf{X} in Euclidean point space. The time is denoted by t . We always assume sufficient regularity to render all subsequent operations meaningful.

We adopt the formulation of the first and second laws of thermodynamics proposed by Gurtin and Williams, which were modified to include surface effects in our previous article. We further admit radiative transfer to the singular surface but require that there be no radiative transfer between separate parts of the body.

The first and second laws assume the following integral form as a consequence of the basic assumptions: for each part \mathcal{P} of \mathcal{B} and each time t

$$\int_{\mathcal{P}} \dot{\epsilon}_{\mathcal{B}}(\mathbf{X}, t) dV(\mathbf{X}) + \int_{\mathcal{P} \cap \mathcal{S}} \dot{\epsilon}_{\mathcal{S}}(\mathbf{X}, t) dA(\mathbf{X}) = \int_{\mathcal{P}} r_{\mathcal{B}}(\mathbf{X}, t) dV(\mathbf{X}) + \int_{\mathcal{P} \cap \mathcal{S}} r_{\mathcal{S}}(\mathbf{X}, t) dA(\mathbf{X}) + \int_{\partial\mathcal{P}} q_{\partial\mathcal{P}}(\mathbf{X}, t) dA(\mathbf{X}) \quad (1)$$

and

$$\int_{\mathcal{P}} \dot{\eta}_{\mathcal{B}}(\mathbf{X}, t) dV(\mathbf{X}) + \int_{\mathcal{P} \cap \mathcal{S}} \dot{\eta}_{\mathcal{S}}(\mathbf{X}, t) dA(\mathbf{X}) \geq \int_{\mathcal{P}} \frac{r_{\mathcal{B}}(\mathbf{X}, t)}{\theta_{\mathcal{B}}(\mathbf{X}, t)} dV(\mathbf{X}) + \int_{\mathcal{P} \cap \mathcal{S}} \frac{r_{\mathcal{S}}(\mathbf{X}, t)}{\theta_{\mathcal{S}}(\mathbf{X}, t)} dA(\mathbf{X}) + \int_{\partial\mathcal{P}} \frac{q_{\partial\mathcal{P}}(\mathbf{X}, t)}{\phi_{\partial\mathcal{P}}(\mathbf{X}, t)} dA(\mathbf{X}). \quad (2)$$

Here $\dot{\epsilon}_{\mathcal{B}}$ and $\dot{\eta}_{\mathcal{B}}$ are the time rates of change of the *internal energy* and *entropy* in \mathcal{B} (per unit volume), $\dot{\epsilon}_{\mathcal{S}}$ and $\dot{\eta}_{\mathcal{S}}$ are the time rates of change of the *internal energy* and *entropy* in \mathcal{S} (per unit area), $r_{\mathcal{B}}$ is the *external radiation* to \mathcal{B} (per unit volume), $r_{\mathcal{S}}$ is the *external radiation* to \mathcal{S} (per unit area), $q_{\partial\mathcal{P}}$ is the *conductive heat flux* through the boundary $\partial\mathcal{P}$ of \mathcal{P} (per unit area), $\theta_{\mathcal{B}}$ is the *volume radiature temperature* in \mathcal{B} , $\theta_{\mathcal{S}}$ is the *surface radiative temperature* in \mathcal{S} , and $\phi_{\partial\mathcal{P}}$ is the *conductive temperature* on the boundary $\partial\mathcal{P}$ of \mathcal{P} . The above inequality may properly be called the extended *Clausius-Duhem* inequality for it reduces, in the absence of surface phenomena on \mathcal{S} , to the generalized Clausius-Duhem inequality exhibited by Gurtin and Williams [6], [8].

The following convention is useful: if $\alpha_{+\hat{\mathcal{S}}}$ and $\alpha_{-\hat{\mathcal{S}}}$ denote quantities associated with the two sides $+\hat{\mathcal{S}}$ and $-\hat{\mathcal{S}}$ of some material surface $\hat{\mathcal{S}}$ in \mathcal{B} , then the *jump in α across $\hat{\mathcal{S}}$* is denoted by $[\alpha]_{\hat{\mathcal{S}}}$ where³

$$[\alpha]_{\hat{\mathcal{S}}} =_{\text{def}} \alpha_{+\hat{\mathcal{S}}} + \alpha_{-\hat{\mathcal{S}}}. \quad (3)$$

Rigorous versions of the classical ‘‘pill box’’ argument yield the following local forms for the first and second laws:

- (i) *the first law: for a material surface $\hat{\mathcal{S}}$ separate from the singular surface \mathcal{S}*

³ The + sign is a consequence of the particular convention used to orient the surface and *jump* should be interpreted in the usual way.

$$[q]_{\hat{s}} = 0 \quad (4)$$

while for the singular surface S

$$[q]_s + r_s = \dot{\epsilon}_s ; \quad (5)$$

(ii) the second law: for a material surface \hat{S} separate from the singular surface S ,

$$[q/\phi]_{\hat{s}} \leq 0 \quad (6)$$

while for the singular surface S

$$[q/\phi]_s + r_s/\theta_s \leq \dot{\eta}_s . \quad (7)$$

Finally, if we define the surface free energy ψ_s on S by

$$\psi_s =_{\text{def}} \epsilon_s - \theta_s \eta_s , \quad (8)$$

the first and second laws imply the following *heat conduction inequality* for the singular surface S :⁴

$$\dot{\psi}_s + \dot{\eta}_s \theta_s \leq [q]_s - \theta_s [q/\phi]_s . \quad (9)$$

II. Constitutive assumptions. In this section we illustrate some constitutive assumptions for singular surfaces. Restrictions on these assumptions imposed by the laws of thermodynamics are then deduced. The method for obtaining these results is by now classical [2], [3] and hence all details are omitted.

Henceforth, in order to simplify our notation, *all explicit dependence upon the singular surface shall be suppressed*. Thus, $q_{\pm s}$ becomes q_{\pm} , $\phi_{\pm s}$ becomes ϕ_{\pm} , ϵ_s becomes ϵ , etc.

Recall that \mathcal{B} is a rigid immobile body. Therefore a material point may be identified with its place \mathbf{X} in some reference configuration and the singular surface S may be identified with a fixed set of material points. This need not be the case for a body and surface in motion. We choose a fixed time interval I and suppose that functions defined on $S \times I$ are sufficiently smooth to ensure that all subsequent operations are valid.

Consider the following functions defined on $S \times I$:

- (i) the *conductive heat flux densities* q_+ and q_- ,
- (ii) the *surface internal energy density* ϵ ,
- (iii) the *surface radiative heat flux density* r ,
- (iv) the *surface internal entropy density* η ,
- (v) the (positive) *conductive temperatures* ϕ_+ and ϕ_- , and
- (vi) the (positive) *surface radiative temperature* θ .

Such a set of eight functions defined on $S \times I$ is called a *surface process* if it is compatible with the first law of thermodynamics, which is equivalent (cf. Eq. (5)) on $S \times I$ to

$$[q] + r = \dot{\epsilon} . \quad (10)$$

The *constitutive assumption* for the singular surface S consists of three parts, the first of which has already been introduced:

- (i) there is no internal radiation in the body;

⁴ The superscript dot indicates material time differentiation.

(ii) every surface process on S is compatible with some thermodynamic process in \mathcal{B} away from S in the sense that the conductive heat fluxes and temperatures on S are identified by the appropriate limits to S from the interior of \mathcal{B} ;

(iii) there exist four response functions $\hat{\epsilon}$, $\hat{\eta}$, \hat{q}_+ , and \hat{q}_- which determine the internal energy ϵ , the internal entropy η , and the conductive heat fluxes q_+ and q_- at any (\mathbf{X}, t) in $S \times I$ whenever the radiative temperature θ , the conductive temperatures ϕ_+ and ϕ_- , and two vectors \mathbf{h}_+ and \mathbf{h}_- are specified at (\mathbf{X}, t) .⁵ Thus we have, for each (\mathbf{X}, t) in $S \times I$, the functions $\epsilon(\mathbf{X}, t)$, $\eta(\mathbf{X}, t)$, $q_+(\mathbf{X}, t)$ and $q_-(\mathbf{X}, t)$ given by

$$\epsilon(\mathbf{X}, t) = \hat{\epsilon}(\theta, \phi_+, \phi_-, \mathbf{h}_+, \mathbf{h}_-), \quad (11a)$$

$$\eta(\mathbf{X}, t) = \hat{\eta}(\theta, \phi_+, \phi_-, \mathbf{h}_+, \mathbf{h}_-) \quad (11b)$$

$$q_+(\mathbf{X}, t) = \hat{q}_+(\theta, \phi_+, \phi_-, \mathbf{h}_+, \mathbf{h}_-), \quad (11c)$$

$$q_-(\mathbf{X}, t) = \hat{q}_-(\theta, \phi_+, \phi_-, \mathbf{h}_+, \mathbf{h}_-). \quad (11d)$$

The functions $\hat{\epsilon}$, $\hat{\eta}$, \hat{q}_+ , and \hat{q}_- are independent of time and assumed to be defined and smooth on $(\mathcal{R}^+)^3 \times \mathcal{U}^2 \times S$, where \mathcal{R}^+ is the positive real line and \mathcal{U} is the translation vector space associated with \mathcal{E} .

Given any choice of temperature fields θ , ϕ_+ , and ϕ_- and vector fields \mathbf{h}_+ and \mathbf{h}_- on $S \times I$, we may always construct a surface process by computing the functions ϵ , η , q_+ , and q_- through (11) and then computing the function r through the first law (10).

We say that a surface process is *admissible* if it is compatible with the constitutive assumption. We require that every admissible surface process be *compatible with thermodynamics*, i.e., that it satisfy the second law of thermodynamics on $S \times I$ (cf. inequality (7)):

$$[q/\phi] + r/\theta \leq \dot{\eta}. \quad (12)$$

If we define the response function for the surface free energy $\hat{\psi}$ by (11a), (11b), and

$$\hat{\psi} = \hat{\epsilon} - \theta \hat{\eta}, \quad (13)$$

and use the heat conduction inequality (9), then we conclude, by means of classical arguments:

(i) the internal energy function $\hat{\epsilon}$, the internal entropy function $\hat{\eta}$, and, hence, the Helmholtz surface free energy function $\hat{\psi}$ depend only upon the surface radiative temperature θ ,

(ii) the internal entropy is determined through the *entropy relation*⁶

$$\hat{\eta}(\theta) = -\partial_\theta \hat{\psi}(\theta); \quad (14)$$

and

(iii) the heat conduction inequality

⁵ The vector functions \mathbf{h}_+ and \mathbf{h}_- on $S \times I$ may be identified with the limits to $+S$ and $-S$ of the gradients of the conductive temperatures in \mathcal{B} whenever such a notion is meaningful, e.g., if the material in \mathcal{B} away from S were a *simple* heat conductor with a smooth temperature field (see Gurtin and Williams [8, §VII]).

⁶ We use ∂_θ to denote differentiation with respect to the variable θ .

$$[q/\phi] \leq \frac{1}{\theta} [q] \quad (15)$$

holds.

We remark here that if the internal energy function is smoothly invertible with respect to the surface radiative temperature, that is, if

$$\partial_\theta \hat{\epsilon} \neq 0, \quad (16)$$

then there exists a *caloric equation of state* for the surface S . That is, there is a function $\bar{\eta}$ of the internal energy ϵ such that

$$\eta = \bar{\eta}(\epsilon). \quad (17)$$

In this case, the *temperature relation* holds:

$$\theta = (\partial_\epsilon \bar{\eta}(\epsilon))^{-1}. \quad (18)$$

By assuming that each conductive heat flux depends upon *both* conductive temperatures as well as the surface radiative temperature, we tacitly assume that the conductive heat flux response functions are not local in character.⁷ At first it might seem reasonable to consider the following modification of the constitutive assumption: the heat flux on a fixed side of the surface S is determined whenever the conductive temperature and the vector parameter associated with that side are specified. Thus (11c) and (11d) are replaced by

$$q_+(\mathbf{X}, t) = \check{q}_+(\phi_+, \mathbf{h}_+), \quad (19a)$$

$$q_-(\mathbf{X}, t) = \check{q}_-(\phi_-, \mathbf{h}_-) \quad (19b)$$

while (11a) and (11b) remain unchanged. It is then easily seen that conclusions (i) and (ii) above regarding the functional dependence of $\hat{\epsilon}$ and $\hat{\eta}$ remain unchanged and that the heat conduction inequality (15) holds. However, (15) together with constitutive assumptions (19a) and (19b) implies that the response functions \check{q}_+ and \check{q}_- vanish; that is, there can be no heat conduction on the singular surface S (!). Therefore this particular violation of the *principle of equipresence* in constitutive assumptions⁸ yields a theory in which the surface cannot interact with the surrounding material.

As a last illustrative example let us consider the case where the surface temperature is a function of the two limiting conductive temperatures. Consistent with the principle of equipresence, we shall assume constitutive relations of the form⁹

$$\epsilon(\mathbf{X}, t) = \hat{\epsilon}(\theta(\phi_+, \phi_-), \phi_+, \phi_-) = \bar{\epsilon}(\phi_+, \phi_-) \quad (20)$$

and similarly for η , q_+ , q_- . Also, we now have

$$\theta(\mathbf{X}, t) = \bar{\theta}(\phi_+, \phi_-). \quad (21)$$

It is a trivial calculation to show that these hypotheses, together with the first and second laws, imply

⁷ For a discussion of local spatial interaction in the thermodynamics of materials, see Gurtin [5] or Coleman and Gurtin [7].

⁸ For a discussion of this notion, see Truesdell and Toupin [1] and Coleman and Gurtin [7].

⁹ For simplicity we shall omit dependence on \mathbf{h}_+ , \mathbf{h}_- as their presence is inconsequential in the present arguments.

$$(i) \quad d\tilde{\psi} = -\eta d\tilde{\theta} \quad (22)$$

and

$$(ii) \quad [\tilde{q}/\phi] \leq \frac{1}{\theta} [\tilde{q}]. \quad (23)$$

For the solution of actual problems these forms may be more convenient than those arising from the independence of θ and ϕ_+ , ϕ_- .

III. Consequences of the heat conduction inequality. In this section we specialize our constitutive assumptions on q_+ , q_- to include only dependence on surface temperature and differences between reciprocal surface temperature and reciprocal conductive temperature limits.¹⁰ Then in a classical manner we are able to use the heat conduction inequality to deduce further restrictions on q_+ , q_- and to also obtain the appropriate linear theory.

We consider a fixed point \mathbf{X} in the singular surface S and a fixed time t such that the temperature $\phi_+ = \phi_+(\mathbf{X}, t)$, $\phi_- = \phi_-(\mathbf{X}, t)$, and $\theta = \theta(\mathbf{X}, t)$ are all defined and positive. All reference to the pair (\mathbf{X}, t) will henceforth be suppressed. Define the reciprocal-temperature differences¹¹ α^+ and α^- by

$$\alpha_+ =_{\text{def}} 1/\phi_+ - 1/\theta, \quad (24a)$$

$$\alpha_- =_{\text{def}} 1/\phi_- - 1/\theta. \quad (24b)$$

It is convenient to associate the pairs (α_+, α_-) and (q_+, q_-) with elements α and \mathbf{q} in \mathcal{R}^2 in the usual way:

$$(\alpha^+, \alpha^-) \leftrightarrow \alpha, \quad (q_+, q_-) \leftrightarrow \mathbf{q}. \quad (25)$$

We make the following

Constitutive assumption. There exists a function¹² ${}^*\mathbf{q}: \mathcal{R}^2 \times \mathcal{R}^{++} \rightarrow \mathcal{R}^2$ of class \mathcal{C}^2 which determines the heat flux as follows: for any triplet of temperatures (ϕ_+, ϕ_-, θ) determine the element (α, θ) in $\mathcal{R}^2 \times \mathcal{R}^{++}$ through (24) and the relation defining α and \mathbf{q} ; then the heat flux is determined through the constitutive equation

$$(\alpha, \theta) \rightsquigarrow \mathbf{q} = {}^*\mathbf{q}(\alpha, \theta). \quad (26)$$

Observe that the point $(\mathbf{0}, \theta)$ in $\mathcal{R}^2 \times \mathcal{R}^{++}$ corresponds to the triplet of temperatures (θ, θ, θ) ; i.e., when $\alpha = \mathbf{0}$ the conductive temperatures are both equal to the surface temperature.

In terms of our notation conventions and the constitutive assumptions, the heat conduction inequality may be written

$${}^*\mathbf{q}(\alpha, \theta) \cdot \alpha \leq 0, \quad (27)$$

¹⁰The formulation in the variables used here was suggested in private communication with M. E. Gurtin.

¹¹ Recall that in the classical continuum theories, the specific entropy production is of the form $\mathbf{h} \cdot \nabla(1/\phi)$ where \mathbf{h} is the heat conduction vector and ϕ is the temperature. See, for example, Truesdell and Noll [4, p. 295].

¹² Of course, the function ${}^*\mathbf{q}$ depends upon the point (\mathbf{X}, t) in general. Also \mathcal{R}^{++} denotes the positive real numbers.

where the dot indicates the standard inner product in \mathcal{R}^2 . From this expression standard arguments [2], [3] yield the following assertions: *if the heat conduction inequality (27) is satisfied,*

(i) *there is no heat flux on S whenever the conductive temperatures ϕ_+ and ϕ_- are both equal to the surface temperature θ :*

$$\mathbf{q}^*(\mathbf{0}, \theta) = \mathbf{0} \quad (28)$$

for each θ in \mathcal{R}^{++} ; and

(ii) *whenever the conductive temperatures ϕ_+ and ϕ_- are both equal to the surface temperature θ , the map $\nabla_{\alpha}^* \mathbf{q}$ in \mathcal{R}^2 is negative semidefinite.*

These assertions and the smoothness of \mathbf{q}^* imply that for each θ in \mathcal{R}^{++} and $|\alpha|$ sufficiently small

$$\mathbf{q}^*(\alpha, \theta) = [\nabla_{\alpha}^* \mathbf{q}(\mathbf{0}, \theta)]\alpha + O(|\alpha|). \quad (29)$$

Hence we have the following linear approximation valid whenever ϕ_+ and ϕ_- are sufficiently close to θ :

$$q_+ = q_+(\alpha_+, \alpha_-, \theta) = k_+^+(\theta)\alpha_+ + k_+^-(\theta)\alpha_-, \quad (30a)$$

$$q_- = q_-(\alpha_+, \alpha_-, \theta) = k_-^+(\theta)\alpha_+ + k_-^-(\theta)\alpha_-, \quad (30b)$$

where the *conductivities* k_+^+ , k_+^- , k_-^+ , and k_-^- satisfy

$$k_+^+(\theta) \leq 0, \quad k_-^-(\theta) \leq 0, \quad \text{and} \quad (k_+^-(\theta) + k_-^+(\theta))^2 \leq 4k_+^+(\theta)k_-^-(\theta), \quad (30c)$$

for all θ in \mathcal{R}^{++} .

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