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An Observation on the Total Energy of a System with Phase Changes

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AN OBSERVATION ON THE TOTAL ENERGY OF A SYSTEM WITH PHASE CHANGES

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ABSTRACT

In most heat transfer processes the choice of a reference energy and reference temperature are arbitrary, since only differences in energy and temperature are relevant to the transfer process. Thus, in applications to thermal energy storage, the total energy of a system will be obtained by integrating the temperature drop relative to an arbitrary reference temperature. In this report we show that the integral of the temperature drop will not yield a physically relevant total energy in a system with a phase change unless the reference point is chosen in a particular fashion. Indeed, we show that conservation of energy constrains us to choose the melt temperature of the material as the reference point in a simple phase change process, while for multiple phase changes (as in iron), or variable melting temperatures (as in the solidification of an alloy), energy conservation places severe restrictions on the choice of the reference point.

Introduction

The most basic condition to be obeyed by a model of a heat transfer process is the conservation of the total energy of the system being modeled. In most cases only differences of energy and temperature play a role, and so both may be referred to an arbitrarily chosen reference state. Thus, for a simple heat transfer process in a slab of length L, one can express the total thermal energy as

$$E(t) = \int_0^L \rho\, c\, [T(x,t) - T_{ref}]\, dx \qquad \text{(Kj/m)}$$

with T_{ref} arbitrary, where ρ is the constant density (kg/m^3), c is the constant specific heat (KJ/kg °C) and T(x,t) is the temperature (°C) at the point x at time t. However, if energy is to be conserved when phase changes and moving boundaries are involved in the model, a straightforward extension of this definition of energy with T_{ref} an arbitrary constant is inappropriate.

The total energy in a body undergoing a phase change is a very important quantity from the practical point of view. Since it must be conserved, it is also very important in the modeling of the process. So, an appropriate definition of the total thermal energy is required. In this report we examine a simple minded but natural definition of energy in various phase change processes. Sections 1 and 2 deal with single and a multiple phase changes respectively in a finite slab. In section 3 we examine the case when the critical temperature varies with time. In all cases we find that the requirement of conservation of energy imposes explicit requirements on the choice of reference

temperature, which sometimes are reasonable and sometimes are not. Results of our search for more appropriate definitions of energy will appear in another report.

An implication of this work is that when computing (either analytically or numerically) energy balances in a material undergoing a phase change one must be careful to choose the reference state so that total energy will be conserved or to modify the definition of total energy appropriately.

1. Energy in a single phase-change process

Let us consider a slab of phase-change material (PCM) occupying the interval $0 < x < L$, initially in its solid state. The slab is insulated at $x = L$ and a heat flux q_0 is applied at $x = 0$ so that the PCM melts at a critical temperature T_{cr}. The interface is a curve $x = X(t)$ such that at time t the liquid occupies $0 < x < X(t)$ and the solid occupies $X(t) < x < L$. Let the constants c_ℓ, k_ℓ and c_s, k_s be the specific heat and conductivity of the liquid and the solid respectively and, for simplicity, let us take the density of the PCM to be a constant, ρ, in both phases.

The standard model for such a process is the following two-phase Stefan problem for the unknown temperature $T(x,t)$ and interface location $X(t)$:

$$\rho c_p T_t = (k_p T_x)_x \quad \text{in the solid } (p=s) \text{ and in the liquid } (p=\ell) \tag{1.1}$$

$$T(X(t), t) = T_{cr}, \tag{1.2}$$

$$\rho H\,\dot{X}(t) = k_s\,T_x(X(t)^+,t) - k_\ell\,T_x(X(t)^-,t) \quad \text{(Stefan condition)}, \tag{1.3}$$

$$-k_\ell T_x\Big|_{x=0} = q_o\,, \quad -k_s\,T_x\Big|_{x=L} = 0. \tag{1.4}$$

In (1.3), H denotes the latent heat of the phase change.

The total energy in the PCM at time t is the energy due to sensible heat and latent heat. A way of expressing this is to write

$$E(t) = \int_0^{X(t)} \rho c_\ell\,[T(x,t) - T_{ref}]\,dx \tag{1.5}$$

$$+ \int_{X(t)}^{L} \rho c_s\,[T(x,t) - T_{ref}]\,dx + \rho H\,X(t).$$

We claim that if the energy is to be conserved, then the reference temperature T_{ref} in <u>this</u> definition of total energy must be taken to be equal to the critical temperature T_{cr}.

Indeed, since the only energy input is q_o, conservation of energy can be expressed as

$$\dot{E}(t) = q_o. \tag{1.6}$$

Differentiating (1.5) with respect to time we find

$$\dot{E}(t) = \rho c_\ell\,[T_{cr} - T_{ref}]\,\dot{X}(t) - \rho c_s\,[T_{cr} - T_{ref}]\,\dot{X}(t)$$

$$+ \int_0^{X(t)} \rho c_\ell\,T_t(x,t)\,dx + \int_{X(t)}^{L} \rho c_s\,T_t(x,t)\,dx + \rho H\,\dot{X}(t).$$

Using (1.1) and integrating by parts, we obtain

$$\dot{E}(t) = \rho(c_\ell - c_s)[T_{cr} - T_{ref}]\,\dot{X}(t) + k_\ell\, T_x\Big|_{x=0}^{x=X(t)} + k_s\, T_x\Big|_{x=X(t)}^{x=L} + \rho H\,\dot{X}(t), \tag{1.7}$$

and then, because of (1.3) and (1.4), we obtain

$$\dot{E}(t) = q_0 + \rho\,(c_\ell - c_s)\,[T_{cr} - T_{ref}]\,\dot{X}(t). \tag{1.8}$$

Therefore, the total energy will be conserved only if the last term in (1.8) vanishes. This term clearly exists because of the phase-change $(c_\ell \neq c_s)$ or the moving boundary $(\dot{X}(t) \neq 0)$. In the presence of such phenomena the only way to make the term vanish is to choose $T_{ref} = T_{cr}$. If the total energy of the system at time t is given by

$$E(t) = \int_0^{X(t)} \rho c_\ell\,[T(x,t) - T_{cr}]\,dx + \int_{X(t)}^{L} \rho c_s\,[T(x,t) - T_{cr}]\,dx + \rho H\,X(t), \tag{1.9}$$

then $\dot{E}(t) = q_0$ and energy is conserved.

Observe that the Stefan condition (1.3) is consistent with definition (1.9) but not with (1.5). Indeed, only when $T_{ref} = T_{cr}$ do (1.6) and (1.7) imply (1.3).

2. Energy in a multiple phase change process.

Let us consider a system in which N distinct phases are created in the PCM which again is insulated at $x = L$ and has a heat flux q_0 imposed at $x = 0$. In each phase the heat conduction equation (1.1) is valid, at each interface $x = X^i(t)$ $(i = 1, 2, \ldots, N-1)$ the temperature is a critical temperature $T^i_{cr}(i = 1, 2, \ldots, N-1)$ and either a Stefan condition of the type (1.3) with latent heat H^i holds there or the fluxes balance each other $k_i\, T^i_x = k_{i+1}\, T^{i+1}_x$ at $x = X^i(t)$; such a condition can occur e.g. when a fast chemical reation takes place at an interface.

We write the total energy as

$$E(t) = \sum_{i=1}^{N} \int_{X^{i-1}(t)}^{X^i(t)} \rho\, c^i\, [T(x,t) - T^i_{ref}]\, dx + \sum_j \rho\, H^j\, X^j(t)$$

where $X^0(t) = 0$, $X^N(t) = L$, c^i is the specific heat of the ith phase, T^i_{ref} is a reference temperature for the ith phase, H^j the latent heat and j takes all the values in $\{1, 2, \ldots, N-1\}$ for which a Stefan condition is prescribed on $x = X^j(t)$.

Proceeding as in section 1, we find that the energy is conserved provided

$$\rho \sum_{i=1}^{N-1} [c^i\, (T^i_{cr} - T^i_{ref}) - c^{i+1}\, (T^i_{cr} - T^{i+1}_{ref})] = 0.$$

Setting each term of this sum equal to zero yields N-1 equations for the N unknowns T^i_{ref}, i=1, 2,..., N. Therefore, there are infinitely many choices for the constants T^i_{ref} which result in conservation of the total energy in such a multiphase system.

3. Energy in a phase change process with time-dependent critical temperature

Let us reconsider now the process of section 1 but allow the critical temperature to be a function of time,

$$T(X(t), t) = T_{cr}(t).$$

Physically this can happen in many interesting situations. For example a chemical reaction may take place at the interface, or there may be simultaneous diffusion of a solute with the critical temperature depending on its concentration

Clearly a constant T_{ref} will not suffice in this case. So, let us take the energy to be given again by (1.5) but with $T_{ref} = T_{ref}(t)$. Computing $\dot{E}(t)$ we find $\dot{E}(t) = \dot{\Omega}(t) + q_0$, with

$$\begin{aligned}\dot{\Omega}(t) &= \rho(c_\ell - c_s)[T_{cr}(t) - T_{ref}(t)]\,\dot{X}(t) - \rho[c_\ell\, X(t) + c_s(L - X(t))]\dot{T}_{ref}(t)\\ &= \rho(c_\ell - c_s)T_{cr}(t)\dot{X}(t) - \rho\,\frac{d}{dt}\,[[c_\ell\, X + c_s(L - X(t))]T_{ref}(t)].\end{aligned}$$

Conservation of energy requires $\dot{\Omega}(t) = 0$, which yields, upon integration, the following expression for the reference temperature:

$$T_{ref}(t) = [c_\ell X(t) + c_s[L - X(t)]]^{-1}\{[c_\ell X(0) + c_s[L - X(0)]]T_{ref}(0)$$

$$+ (c_\ell - c_s) \int_0^t T_{cr}(\tau)\dot{X}(\tau)d\tau\}.$$

Note that the denominator is never zero, so $T_{ref}(t)$ is well-defined. Alternatively, integrating by parts in the last integral and, choosing $T_{ref}(0) = T_{cr}(0)$, we find

$$T_{ref}(t) = [c_s + (c_\ell - c_s)\ X(t)]^{-1}\{c_s\ T_{cr}(0) + (c_\ell - c_s)T_{cr}(t)\ X(t)$$

$$- (c_\ell - c_s) \int_0^t X(\tau)\ \dot{T}_{cr}(\tau)d\tau\}.$$

For convenience we define $\mu = c_s/(c_\ell - c_s)$. Then

$$T_{ref}(t) = [\mu + X(t)]^{-1}\ \{\mu\ T_{cr}(0) + T_{cr}(t) - \int_0^t X(\tau)\ \dot{T}_{cr}(\tau)d\tau\}. \quad (3.2)$$

Thus, the total energy in the system may be defined by

$$E(t) = \int_0^{X(t)} \rho c_\ell[T(x,t) - T_{ref}(t)]dx + \int_{X(t)}^{L} \rho c_s[T(x,t) - T_{ref}(t)]dx$$

$$+ \rho\ H\ X(t), \quad (3.3)$$

with T_{ref} (t) as given above.

Unfortunately, a variable T_{ref} cannot be used as a reference temperature in physical measurements, so (3.3) as a definition of energy is not satisfactory from the physical point of view.

An alternative to having a time-dependent reference temperature is to choose an arbitrary constant T_0 as the reference temperature and compensate by adding a "source" term in the definition of energy so that the latter will be conserved. Clearly, the term to be added must be equal to $-\dot{\Omega}(t)$ with $T_{ref}(t) \equiv T_0 = \text{const.}$ Thus the modified definition of total energy is

$$E(t) = \int_0^{X(t)} \rho c_\ell [T(x,t) - T_0] dx + \int_{X(t)}^{L} \rho c_s [T(x,t) - T_0] dx + \rho H X(t)$$

$$+ \rho (c_s - c_\ell) \int_0^t [T_{cr}(t) - T_0] \dot{X}(t) dt. \qquad (3.4)$$

<u>Remark</u> If the critical temperature happens to be a constant, then (3.1) (or (3.2)) simply says $T_{ref}(t) = T_{cr} = \text{const.}$, and (3.3) as well as (3.4) reduce to (1.8), thus recovering the results of section 1.

The difficulty with the modified definition (3.4) is that its last term cannot be interpreted physically in any reasonable way. Clearly, a more appropriate definition of total energy is needed. This will be addressed in a forthcoming report.

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