

Phase Transitions in Materials with Thermal Memory: a Summary of Recent Results

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Abstract

A model for thermally induced phase transitions in rigid materials with thermal memory was recently proposed, both for the case where the phases have the same conductivity properties and where they are different. Various results were derived from asymptotic analysis of the relevant integro-partial differential equations. In particular, a relation is given connecting the discontinuity in the temperature field over the transition zone with the normal velocity of the transition zone. The latent heat must depend on this velocity and becomes negligible compared with the specific heat as it approaches either of the speeds of propagation of thermal disturbances. There is also a condition which is different from the Stefan condition connecting temperature gradient values on either side of the transition zone with velocity, but which reduces to this form in the low transition zone velocity limit.

The model was also extended to the case of heat flow relations which include instantaneous contributions of the Fourier type as well as memory terms. Asymptotic analysis in this case yields results very similar to those for the classical theory without memory, namely no discontinuity in the temperature field and the Stefan condition.

1 Introduction

There have been two approaches to the macroscopic modelling of phase transitions.

In the first, the transition zone is visualized as a surface of discontinuity or sharp interface with no thickness, though it may have interfacial structure. In the second approach, the transition zone is assumed to have finite thickness. It is characterized by a phase field or order parameter which is constant in the bulk materials and varies rapidly across the transition zone. The foundation of this method is the Ginzburg-Landau theory of superconductivity.

We present here a brief review of recent work [1, 2, 3] using asymptotic analysis of the integro-partial differential equations describing materials with thermal memory. These governing equations were derived by systematic arguments based on thermodynamics [1, 2], generalizing an approach by Fried and Gurtin [4] for materials without thermal memory. The asymptotic analysis technique is as developed in [5, 6], though the presence of memory causes extra difficulties.

Asymptotic analysis applied to temperature driven phase transitions without

memory (Fourier theory), using a phase field description yields [6]

1. a temperature field that is continuous across the transition zone \mathcal{Z} ;
2. the Stefan condition: Discontinuity of heat flux (conductivity \times normal derivative of temperature) across \mathcal{Z} = velocity of transition zone \times latent heat;
3. a modified Gibbs-Thomson relation.

In [1], these results were generalized to materials with thermal conductivity described by a memory kernel, where both phases were assumed to have the same conductivity properties. There was no instantaneous Fourier term. The resulting equations are related to and generalize those developed in [7], specifically the linear version, which in turn generalizes [8]. These theories predicts finite velocities of thermal disturbances, in contrast to the classical Fourier theory and therefore must be regarded as more physical than the Fourier theory, though the latter is frequently used in practical applications.

In [2], the asymptotic analysis was extended to materials with heat conductivity properties described by a memory kernel that was different for each of the phases. Certain aspects of this model proved considerably more complicated but the results were straightforward and natural generalizations of the single conductivity theory.

Interesting results were obtained in both of these cases. In particular, a relation was given connecting the discontinuity in the temperature field over the transition zone with the normal velocity of the transition zone. To avoid singularities in the temperature field, it was argued that the latent heat must depend on this velocity and becomes negligible compared with the specific heat as it approaches either of the speeds of propagation of thermal disturbances. There was also a relation different from the Stefan condition connecting the values of the temperature gradient on either side of the transition zone with velocity, but which reduces to this form in the low transition zone velocity limit.

Finally, in [3], a model was analysed where, as well as memory contributions, Fourier terms were also present, which greatly effect the results. What emerges from the asymptotic analysis are features similar to those for the theory without memory as listed above. By introducing such instantaneous Fourier terms, we of course return to the problematic feature of infinite speeds of thermal disturbances.

2 Field equations

Let θ be the absolute temperature and θ_M the transition temperature. We introduce the quantity

$$u = \frac{\theta - \theta_M}{\theta_M}$$

which is assumed to be small. The temperature gradient is given by

$$\mathbf{g} = \nabla\theta$$

The phase field is denoted by φ where

$$\varphi(\mathbf{x}, t) = \begin{cases} 1, & \text{(solid phase)} \\ 0, & \text{(liquid phase)}. \end{cases}$$

It varies rapidly from zero to one over the transition zone \mathcal{Z} . A central feature of the phase field approach is the presence of a double well potential $\nu f(\varphi)$, allowing two stable states, solid and liquid.

Consider a function $h(\phi)$ with the properties

$$h(1) = 1, \quad h(0) = 0$$

which is assumed to be invertible on the interval $(0, 1)$. For example, we could put $h(\varphi) = \varphi^n$, $n > 0$. The theory can be developed without specifying a particular form. Define

$$\mathbf{g}_l = (1 - h)\mathbf{g}, \quad \mathbf{g}_s = h\mathbf{g}.$$

so that \mathbf{g}_l is equal to \mathbf{g} on the liquid phase and zero on the solid phase. The reverse is true for \mathbf{g}_s .

The standard notation

$$F^t(s) = F(t - s)$$

is used below.

After many simplifications [1, 2, 3], the field equations (phase field and heat equations) in non-dimensional form become

$$\begin{aligned} \alpha \epsilon^2 \dot{\varphi} &= \epsilon^2 \Delta \varphi - f'(\varphi) - u \beta \epsilon g'(\varphi) \\ \dot{u} &= \gamma \dot{g}(\varphi) + \nabla \cdot [(K_l h_l + K_s h_s) \nabla u] \\ &+ \nabla \cdot (k_l \circ h_l^t \nabla u^t) + \nabla \cdot (k_s \circ h_s^t \nabla u^t), \end{aligned} \quad (1)$$

where

$$\begin{aligned} k_l \circ h_l^t \nabla u^t &= \int_0^\infty k_l(s) h_l^t(s) \nabla u^t(s) ds \\ &= \int_{-\infty}^t k_l(t - s) h_l(s) \nabla u(s) ds, \end{aligned}$$

and similarly for $k_s \circ h_s^t \nabla u^t$. The quantities k_l , k_s are the dimensionless thermal memory kernels and

$$\beta \epsilon = \frac{\lambda}{\nu}, \quad \gamma = \frac{\lambda}{\theta_M c}, \quad \epsilon \ll 1 \quad (2)$$

in terms of the latent heat λ , the specific heat c and the height of the double well potential ν . The parameter α is a constant defined in [1]. The symbol Δ is the three-dimensional Laplacian. Equations (1) are based on relations derived from thermodynamical considerations in [1] and generalized in [2].

The functions f and g are often chosen as

$$f(\varphi) = \frac{1}{2}\varphi^2(1 - \varphi)^2, \quad g(\varphi) = \varphi^2(3 - 2\varphi).$$

The quantity f is the double-well potential, alluded to above. This choice of f is the simplest form of a double-well potential with minima at $\varphi = 0$ and $\varphi = 1$. The quantity g must obey

$$g(1) - g(0) = 1, \tag{3}$$

a property also required of $h(\varphi)$. The relationship between $g(\phi)$ and $h(\phi)$ plays an interesting role in the theory developed in [2]. The simplest case is where they are the same function. The choice of these two functions no doubt has some measurable physical consequences, which are however probably small.

The thermal conductivities K_l and K_s for the liquid and solid phases respectively, which are included in (1), characterize the Fourier terms introduced in [3] but excluded in the earlier work [1, 2]. The problem of infinite speeds of propagation of thermal disturbances in the two phases arises again if these are included, as noted earlier. In spite of this, the effect of inclusion of these terms is certainly worth exploring, if only because of the use of classical Fourier theory in a wide variety of contexts.

In the absence of such instantaneous contributions, the speeds of propagation of thermal disturbances in the two phases [7] are given in dimensionless form by

$$V_l = \sqrt{k_l(0)}, \quad V_s = \sqrt{k_s(0)}.$$

The transition zone \mathcal{Z} is defined as

$$\mathcal{Z} = \{\mathbf{x} : \varphi(\mathbf{x}, t) \in [0, 1]\}.$$

3 Steady-state case

In [1, 2], asymptotic analysis was carried out both in the general case where the transition zone is moving and changing shape in a time and position dependent way and for the case where the transition zone has fixed shape and moves at constant velocity because steady state conditions have been established everywhere in the medium. Only the latter model was analysed in [3] and will be considered here. Thus, we assume that

$$-\mathbf{V} = -(V_x, V_y, V_z), \quad V_x > 0$$

and that steady-state conditions have been established over the entire body. The solid, for which $\varphi = 1$, is on the positive side and the liquid, for which $\varphi = 0$, is on the negative side. The field equations can be written in a frame moving with

the transition zone. Explicit time dependence drops out and we obtain

$$\begin{aligned}
\alpha\epsilon^2\mathbf{V}\cdot\nabla\varphi &= \epsilon^2\Delta\varphi - f'(\varphi) - u\beta\epsilon g'(\varphi) \\
\mathbf{V}\cdot\nabla u &= \gamma\mathbf{V}\cdot\nabla g(\varphi) \\
&+ \nabla\cdot[(K_l h_l + K_s h_s)\nabla u] \\
&+ \nabla\cdot\int_0^\infty k_l(s)h_l(\mathbf{x}-\mathbf{V}s)\nabla u(\mathbf{x}-\mathbf{V}s)ds \\
&+ \nabla\cdot\int_0^\infty k_s(s)h_s(\mathbf{x}-\mathbf{V}s)\nabla u(\mathbf{x}-\mathbf{V}s)ds, \\
\phi &= \phi(x, y, z) = \phi(\mathbf{x}), \quad u = u(x, y, z) = u(\mathbf{x}).
\end{aligned}$$

The transition zone \mathcal{Z} is fixed in this frame. For definiteness, a particular surface \mathcal{S} through \mathcal{Z} is chosen as a reference interface. The origin of space coordinates is assumed to be on this interface. The coordinate axis is oriented so that the x direction is normal to \mathcal{S} and the yz plane is tangential to this surface.

We can approximate u in the transition zone by

$$u(x, y, z) = u(x, 0, 0) - u_x(x, 0, 0) \left(\frac{y^2}{2R_y} + \frac{z^2}{2R_z} \right),$$

where R_y, R_z are the radii of curvature of \mathcal{S} at the origin. Note that

$$\Delta_2 u(x, y, z) = -u_x(x, 0, 0)\mathcal{K}_0,$$

where

$$\Delta_2 = \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}.$$

and where \mathcal{K}_0 is given by

$$\mathcal{K}_0 = \frac{1}{R_y} + \frac{1}{R_z}. \quad (4)$$

It is a measure of the curvature of the transition zone at the origin.

4 Asymptotic analysis

For $\mathbf{x} = (x, y, z)$ in \mathcal{Z} we replace x by

$$r = \frac{x}{\epsilon}.$$

which magnifies the transition zone. Thus, $\frac{\partial\varphi}{\partial x}$ is very large in \mathcal{Z} while $\frac{\partial\varphi}{\partial r} = \epsilon\frac{\partial\varphi}{\partial x}$ is $O(1)$. Let

$$u(r, y, z) = u_0(r, y, z) + \epsilon u_1(r, y, z) + O(\epsilon^2),$$

inside the transition zone, and

$$\bar{u}(x, y, z) = \bar{u}_0(x, y, z) + \epsilon \bar{u}_1(x, y, z) + O(\epsilon^2)$$

outside of \mathcal{Z} . The matching condition on u is

$$u(x/\epsilon, y, z) = u(r, y, z) = \bar{u}(\epsilon r, y, z)$$

for large r and ϵr in the vicinity of the edges of \mathcal{Z} , which gives, on putting $\epsilon = 0$,

$$u_0(\pm\infty, y, z) = \bar{u}_0(0\pm, y, z).$$

and (subscripts r, x denote differentiation)

$$\begin{aligned} u_{0r}(\pm\infty, y, z) &= 0, \\ u_{1r}(\pm\infty, y, z) &= \bar{u}_{0x}(0\pm, y, z), \\ u_{0rr}(\pm\infty, y, z) &= 0 \text{ etc.} \end{aligned} \tag{5}$$

The functions $\bar{u}_0(0\pm, y, z)$, $\bar{u}_{0x}(0\pm, y, z)$ are the boundary values of these quantities on the positive and negative sides of \mathcal{Z} .

A similar, though simpler, procedure can be carried out for the phase field [1, 2].

Asymptotic analysis techniques allow us to solve the field equations in the transition zone for leading orders.

5 The heat equation

Putting

$$\begin{aligned} [u_0]_- &= u_0(\infty, y, z) - u_0(-\infty, y, z) \\ &= \bar{u}_0(0+, y, z) - \bar{u}_0(0-, y, z), \end{aligned} \tag{6}$$

the $O(\epsilon)$ relations in [2] give

$$\begin{aligned} [u_0]_- &= [\bar{u}_0]_- = \frac{V_x^2 \gamma}{V_x^2 - V_J^2}, \\ V_J^2 &= V_s^2(1 - J(V_x)) + V_l^2 J(V_x) \end{aligned} \tag{7}$$

relating the discontinuity in the temperature field and the velocity. The quantity $J(V_x)$ depends on the relationship between $h(\varphi)$ and $g(\varphi)$. For V_x near V_s , the quantity V_J approaches V_s also, so that there is a singularity at this value. Similarly, we have singular behaviour when V_x approaches V_l . To avoid singularities in the temperature field, we must assume that γ , defined by (2), depends on V_x and goes to zero as V_x approaches V_l or V_s .

With Fourier terms present, we obtain from the $O(1)$ analysis [3]

$$[u_0]_- = 0, \tag{8}$$

which is the same as for classical Fourier theory without memory.

The $O(\epsilon^2)$ relations in [2] give

$$\begin{aligned} & (V_x^2 - V_s^2)\bar{u}_{0x}(0+) - (V_x^2 - V_l^2)\bar{u}_{0x}(0-) \\ &= \frac{1}{V_x}C_J(0)[\bar{u}_0]_- = \frac{C_J(0)V_x\gamma(\mathbf{V})}{V_x^2 - V_J^2}, \end{aligned} \quad (9)$$

where \mathcal{K}_0 is defined by (4) and

$$C_i(s) = k'_i(s) - V_x\mathcal{K}_0k_i(s), \quad i = l, s. \quad (10)$$

With the Fourier terms present, we obtain from $O(\epsilon)$ terms the form of the classical Stefan relation [3]

$$\begin{aligned} & K_s u_{1r}(\infty) - K_l u_{1r}(-\infty) \\ &= K_s \bar{u}_{0x}(0+) - K_l \bar{u}_{0x}(0-) = -V_x\gamma, \end{aligned} \quad (11)$$

where (5)₂ has been invoked. Thus, to $O(\epsilon)$ in this theory, the classical (no memory) results apply.

To $O(\epsilon^2)$, when the Fourier terms are present, we obtain [3]

$$\begin{aligned} & V_x K_s \bar{u}_{0xx}(0+) - V_x K_l \bar{u}_{0xx}(0-) \\ & - (V_x^2 - V_s^2 + V_x \mathcal{K}_0 K_s) \bar{u}_{0x}(0+) \\ & + (V_x^2 - V_l^2 + V_x \mathcal{K}_0 K_l) \bar{u}_{0x}(0-) = 0. \end{aligned} \quad (12)$$

The quantities V_s^2 and V_l^2 , which are equal to $k_s(0)$ and $k_l(0)$ respectively, represent the contributions of the memory terms, indeed the first such explicit contributions in the theory under discussion.

In the case where the conductivity properties are the same in both phases, we have $V_l = V_s = V_J = V_h$ and $K_l = K_s = K$, where V_h and K are the unique velocity of thermal disturbance and unique Fourier conductivity respectively. Relations (7), (9), (11) and (12) simplify accordingly, reducing indeed to terms involving the jumps in the derivatives of the temperature field across the transition zone. The relevant expressions for the case where $K_l = K_s = 0$ are given in [1].

The results which emerge from [1, 2], without the Fourier terms, are more realistic, from a physical point of view, than those from [3] because of the finite speeds of thermal disturbances. They are also more interesting, in particular with respect to the prediction regarding γ .

6 Phase field equation

An asymptotic analysis of the phase field equation yields [1]

$$\begin{aligned} u_{av} &= -\frac{\sigma}{\lambda}(\alpha V_x + \mathcal{K}_0) \\ u_{av} &= \int_{-\infty}^{\infty} u_0(r') g_r(\varphi_0(r')) dr' \end{aligned}$$

noting that, by virtue of (3),

$$\int_{-\infty}^{\infty} g_r(\varphi_0(r')) dr' = 1$$

The quantity u_{av} is an average of $u_0(r)$ across the transition zone. Also, σ is the surface tension.

This is a modified Gibbs-Thomson boundary condition for the material under consideration, resembling that which emerges from the theory without memory, which is not unexpected since the memory kernels occur only in the heat equation.

7 The steady-state heat equation outside \mathcal{Z}

We now discuss how the macroscopic heat equations are affected by the transition zone. Let us adopt the notation u instead of \bar{u} for dimensionless temperature fields outside the transition zone.

In the liquid phase (which, in fixed coordinates, is ablating) we have simply

$$\mathbf{V} \cdot \nabla u = K_l \Delta u(\mathbf{x}) + \Delta \int_0^{\infty} k_l(s) u(\mathbf{x} - \mathbf{V}s) ds.$$

and the heat flux equation is given by

$$\mathbf{q}(\mathbf{x}) = -K_l \nabla u(\mathbf{x}) - \nabla \int_0^{\infty} k_l(s) u(\mathbf{x} - \mathbf{V}s) ds.$$

For $\mathbf{x} = (x, y, z)$ in the solid phase, the situation is more complicated. Let the quantity $\tau(\mathbf{x})$ be the time period elapsed since the surface \mathcal{S} , passing through the origin, crossed \mathbf{x} . Also, τ_{\pm} are the limits to τ from above and below.

The heat equation has the form

$$\begin{aligned} \mathbf{V} \cdot \nabla u &= K_s \Delta u(\mathbf{x}) + \int_0^{\tau_-(\mathbf{x})} k_s(s) \Delta u(\mathbf{x} - \mathbf{V}s) ds \\ &\quad + \int_{\tau_+(\mathbf{x})}^{\infty} k_l(s) \Delta u(\mathbf{x} - \mathbf{V}s) ds + j(\mathbf{x}), \\ j(\mathbf{x}) &= \frac{C_J}{V_x^2} [u]_- + \frac{1}{V_x} (k_s(\tau) u_x(\mathbf{x} - \mathbf{V}s)|_{s=\tau_-(\mathbf{x})} \\ &\quad - k_l(\tau) u_x(\mathbf{x} - \mathbf{V}s)|_{s=\tau_+(\mathbf{x})}), \\ [u]_- &= u(\mathbf{x} - \mathbf{V}\tau_-) - u(\mathbf{x} - \mathbf{V}\tau_+), \\ C_J(\tau) &= (1 - J)C_s(\tau) + JC_l(\tau), \end{aligned} \tag{13}$$

in terms of the notation of (10).

For $s > \tau$, u is the solution of the liquid zone equation. These relations are thus an inter-related system of integro-partial differential equations, to be solved subject to suitable boundary conditions.

The equation for the heat flux in the solid phase can be written as

$$\begin{aligned}
\mathbf{q}(\mathbf{x}) &= -K_s \nabla u(\mathbf{x}) - \int_0^{\tau^-(\mathbf{x})} k_s(s) \nabla u(\mathbf{x} - \mathbf{V}s) ds \\
&\quad - \int_{\tau_+(\mathbf{x})}^{\infty} k_l(s) \nabla u(\mathbf{x} - \mathbf{V}s) ds - k_J(\tau) \nabla \tau [u]_- \\
&= -K_s \nabla u(\mathbf{x}) - \nabla \int_0^{\infty} k(s) u(\mathbf{x} - \mathbf{V}s) ds \\
&\quad + \frac{1}{2} \nabla \tau (k_s(\tau) - k_l(\tau)) [u]_J, \\
k_J(\tau) &= k_s(\tau)(1 - J) + k_l(\tau)J \\
[u]_J &= 2[u(\mathbf{x} - \mathbf{V}\tau_-)J + u(\mathbf{x} - \mathbf{V}\tau_+)(1 - J)]
\end{aligned} \tag{14}$$

where $k : \mathcal{R}^+ \mapsto \mathcal{R}$ is defined by

$$\begin{aligned}
k(s) &= k_l(s), \quad s > \tau(\mathbf{x}) \\
&= k_s(s), \quad s < \tau(\mathbf{x}).
\end{aligned}$$

The quantity $\nabla \tau$ in (14) can be approximated by [1]

$$\nabla \tau = \frac{1}{V_x} (1, 0, 0),$$

so that y and z components of terms proportional to it can be neglected. We have included the Fourier terms. If these are zero, $[u]_-$ is given by (7), while if they are non-zero, it vanishes, in accordance with (8) so that the expression for $j(\mathbf{x})$ in (13) and the non-integral terms in (14) become simpler.

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