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Anna Maria Caucci and Michel Frémond

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THERMAL EFFECTS OF COLLISIONS: DOES RAIN TURN INTO ICE WHEN IT FALLS ON FROZEN GROUND?

ANNA MARIA CAUCCI AND MICHEL FRÉMOND

Dedicated to H. D. Bui, V. K. Dang, G. Del Piero, J. Salençon, J. Zarka.

The phase changes produced by the thermal effects of collisions are investigated. The behaviour of warm rain falling on a deeply frozen ground is predicted. The ice-water phase change involves microscopic motions that are taken into account in the predictive theory.

1. Introduction

Consider warm rain falling on frozen ground, or hailstones falling on warm ground. We will investigate the thermal consequences of such collisions. Does the rain freeze, turning into the "black ice" that can make paved roads so hazardous in winter? Does the hailstone melt? We will investigate these very fast phase changes due to collisions, providing a scheme for the thermomechanical theory of collisions involving phase change.

The classical ice-water phase change involves microscopic motions, which, in our view, must be taken into account in the macroscopic predictive theory. The basic idea we have developed is to account for the power of the microscopic motions in the power of the interior forces [Frémond 2001; 2007]. We modify the expression of the power of the interior forces and assume it depends on the liquid water volume fraction velocity, $d\beta/dt$, which is clearly related to microscopic motion. The consequences of this assumption give the basic equations of motion, one for macroscopic motion and another for microscopic motion.

We assume the collisions are instantaneous, and thus it is wise to assume that the resulting phase changes are also instantaneous; the very fast evolution of the liquid water volume fraction β is described by a discontinuity with respect to time. The discontinuities of the liquid water volume fraction $[\beta]$ intervene in nonsmooth equations of motion, accounting for microscopic motion. Moreover, when phase change occurs, the temperatures are discontinuous with respect to time.

In Section 2, we derive the equations of motion for a collision of two balls of ice. The balance laws are given in Section 3 and the constitutive laws in Section 4. In Section 5, examples of phase changes produced by the thermal effects of collisions are described: the collision of two pieces of ice (Section 5.2), and the collision of a warm droplet of rain falling on frozen ground (Section 6).

2. The equations of motion

Let us consider the system made of two balls of ice, $\mathcal{B}_1$ and $\mathcal{B}_2$, which move along an axis and collide. Note that such a system is deformable, because the relative position of the balls changes. For the sake

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of simplicity, we assume the balls to be points. We restrict our investigation of the motion and of the thermal evolution to collisions of the two balls. The smooth evolution is straightforward.

In the following discussion, we use indices $_1$ and $_2$ to denote physical quantities relative to the balls $\mathcal{B}_1$ and $\mathcal{B}_2$. The indices $^-$ and $^+$ are used to designate the quantities before and after the collision. The time discontinuity of a function $t \mapsto \mathcal{A}(t)$ is denoted by

$$[\mathcal{A}] = \mathcal{A}^+ - \mathcal{A}^-.$$

The equations of motion are derived from the principle of virtual work which introduces different contributions: the virtual works of the acceleration, interior, and exterior forces [Frémond 2001; 2007].

The virtual work of the acceleration forces is

$$\mathcal{T}^{\mathrm{acc}}(\boldsymbol{U}, \boldsymbol{V}) = m_1[\boldsymbol{U}_1]\frac{\boldsymbol{V}_1^+ + \boldsymbol{V}_1^-}{2} + m_2[\boldsymbol{U}_2]\frac{\boldsymbol{V}_2^+ + \boldsymbol{V}_2^-}{2},$$

where m_1 and m_2 are the masses of the two balls, $\boldsymbol{U} = (\boldsymbol{U}_1, \boldsymbol{U}_2)$ their actual velocities, and $\boldsymbol{V} = (\boldsymbol{V}_1, \boldsymbol{V}_2)$ are the macroscopic virtual velocities.

The virtual work of the interior forces, $\mathcal{T}^{\mathrm{int}}$, is a linear function of the virtual velocity fields; in particular, it is chosen to depend on the system velocity of deformation, $D(\boldsymbol{V}) = \boldsymbol{V}_1 - \boldsymbol{V}_2$, and also on $[\delta] = ([\delta_1], [\delta_2])$, where δ_1 and δ_2 are the virtual liquid water volume fractions of the two balls in the ice-water phase change, the actual volume fractions being β_1 and β_2. It is worth noting that $[\delta_i] = (\delta_i^+ - \delta_i^-)$, $i = 1, 2$, is analogous to $\mathrm{d}\delta_i/\mathrm{d}t$, which represents, in a smooth evolution, a virtual velocity of phase change. This latter quantity is clearly related to microscopic motion.

We choose the virtual work of the interior forces as

$$\mathcal{T}^{\mathrm{int}}\big(D(\boldsymbol{V}), [\delta]\big) = -P^{\mathrm{int}} D\Big(\frac{\boldsymbol{V}^+ + \boldsymbol{V}^-}{2}\Big) - A_1[\delta_1] - A_2[\delta_2],$$

where P^{int} is the interior percussion that intervenes when collisions occur, and $A = (A_1, A_2)$ are the interior microscopic works.

Assuming no exterior percussion, for instance when there is no hammer stroke, and no exterior electrical, radiative, or chemical impulse, the virtual work of the exterior forces is $\mathcal{T}^{\mathrm{ext}}(\boldsymbol{V}) = 0$.

The principle of virtual work,

$$\forall \boldsymbol{V}, [\delta] : \quad \mathcal{T}^{\mathrm{acc}}(\boldsymbol{V}) = \mathcal{T}^{\mathrm{int}}\big(D(\boldsymbol{V}), [\delta]\big),$$

gives easily the equations of motion

$$m_1[\boldsymbol{U}_1] = -P^{\mathrm{int}}, \qquad m_2[\boldsymbol{U}_2] = P^{\mathrm{int}} \tag{2-1}$$

$$A_1 = 0, \qquad A_2 = 0. \tag{2-2}$$

Remark 2.1. We have assumed that there is no exterior impulse inducing phase change. In case there is one, for instance an electrical impulse, or a chemical impulse able to produce a phase change, A_1^{ext}, the equation of motion (2-2) becomes $A_1 = A_1^{\mathrm{ext}}$.

3. The laws of thermodynamics

The laws of thermodynamics are the same for the two balls.

3.1. ***The first law.*** We first consider each ball separately. For $\mathcal{B}_1$, the first law of thermodynamics is

$$[\mathcal{E}_1]+[\mathcal{K}_1]=\mathcal{T}_1^{\mathrm{ext}}(\boldsymbol{U})+\mathcal{C}_1, \tag{3-1}$$

where $\mathcal{E}_1$ is the internal energy of the ball, $\mathcal{K}_1$ its kinetic energy, $\mathcal{T}_1^{\mathrm{ext}}(\boldsymbol{U})$ the actual work of the percussions which are exterior to ball $\mathcal{B}_1$, and $\mathcal{C}_1=T_1^+(B_1^+ + B_{12}^+)+T_1^-(B_1^- + B_{12}^-)$ the heat impulse provided to the ball at the time of collision. This quantity includes the heats T_1B_1 received from outside the system, and the heats T_1B_{12} received from inside, that is, from the other ball. We assume that these heats are received at a temperature of either T_1^+ or T_1^-.

The theorem of kinetic energy for ball $\mathcal{B}_1$ is

$$[\mathcal{K}_1]=\mathcal{T}_1^{\mathrm{acc}}(\boldsymbol{U})=\mathcal{T}_1^{\mathrm{int}}([\beta_1])+\mathcal{T}_1^{\mathrm{ext}}(\boldsymbol{U})=-A_1[\beta_1]+\mathcal{T}_1^{\mathrm{ext}}(\boldsymbol{U}),$$

with $\mathcal{T}_1^{\mathrm{int}}([\delta_1])=-A_1[\delta_1]$. It gives, with the first law of thermodynamics (3-1),

$$\begin{aligned}[\mathcal{E}_1] &= \mathcal{C}_1-\mathcal{T}_1^{\mathrm{int}}([\beta_1]) = T_1^+(B_1^+ + B_{12}^+)+T_1^-(B_1^- + B_{12}^-)+A_1[\beta_1]\\ &= \overline{T}_1(\Sigma B_1+\Sigma B_{12})+[T_1](\Delta B_1+\Delta B_{12})+A_1[\beta_1],\end{aligned} \tag{3-2}$$

with the notations

$$\overline{T}=\frac{T^+ + T^-}{2},\qquad \Sigma B=B^+ + B^-,\qquad \Delta B=\frac{B^+ - B^-}{2},$$

retained in the sequel.

Now we consider the system as a whole. The internal energy of the system is the sum of the internal energies of its components, $\mathcal{E}_1$ and $\mathcal{E}_2$, to which an interaction internal energy, $\mathcal{E}^{\mathrm{int}}$, may be added, giving $\mathcal{E}=\mathcal{E}_1+\mathcal{E}_2+\mathcal{E}^{\mathrm{int}}$.

The first law of thermodynamics for the system is $[\mathcal{E}]+[\mathcal{K}]=\mathcal{T}^{\mathrm{ext}}(\boldsymbol{U})+\mathcal{C}$, where $\mathcal{K}$ is the kinetic energy of the whole system and $\mathcal{C}$ is the exterior heat impulse received by the system in collision, given by $\mathcal{C}=T_1^+B_1^+ + T_1^-B_1^- + T_2^+B_2^+ + T_2^-B_2^-$.

The theorem of kinetic energy, that is, the principle of virtual power with the actual velocities

$$[\mathcal{K}]=\mathcal{T}^{\mathrm{acc}}(\boldsymbol{U})=\mathcal{T}^{\mathrm{int}}\big(D(\boldsymbol{U}),[\beta_1],[\beta_2]\big)+\mathcal{T}^{\mathrm{ext}}(\boldsymbol{U}),$$

and the first law of thermodynamics gives

$$[\mathcal{E}]=\mathcal{C}-\mathcal{T}^{\mathrm{int}}\big(D(\boldsymbol{U}),[\beta_1],[\beta_2]\big)=\mathcal{C}+P^{\mathrm{int}}D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big)+A_1[\beta_1]+A_2[\beta_2]. \tag{3-3}$$

Combining (3-2) and (3-3) we obtain

$$\begin{aligned}[\mathcal{E}] &= [\mathcal{E}_1]+[\mathcal{E}_2]+[\mathcal{E}^{\mathrm{int}}]\\ &= \overline{T}_1(\Sigma B_1+\Sigma B_{12})+[T_1](\Delta B_1+\Delta B_{12})+A_1[\beta_1]\\ &\qquad + \overline{T}_2(\Sigma B_2+\Sigma B_{21})+[T_2](\Delta B_2+\Delta B_{21})+A_2[\beta_2]+[\mathcal{E}^{\mathrm{int}}]\\ &= T_1^+B_1^+ + T_1^-B_1^- + T_2^+B_2^+ + T_2^-B_2^- + P^{\mathrm{int}}D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big)+A_1[\beta_1]+A_2[\beta_2]\\ &= \overline{T}_1\Sigma B_1+[T_1]\Delta B_1+\overline{T}_2\Sigma B_2+[T_2]\Delta B_2+P^{\mathrm{int}}D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big)+A_1[\beta_1]+A_2[\beta_2].\end{aligned}$$

Then

$$[\mathscr{E}^{\text{int}}] = P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - \overline{T}_1 \Sigma B_{12} - [T_1]\Delta B_{12} - \overline{T}_2 \Sigma B_{21} - [T_2]\Delta B_{21}. \tag{3-4}$$

This relationship is interesting because only interior quantities intervene.

3.2. ***The second law of thermodynamics.*** Again we start with each ball separately. Let $\mathscr{S}_1$ be the entropy of ball $\mathscr{B}_1$. The second law of thermodynamics is

$$[\mathscr{S}_1] \geq B_1^+ + B_1^- + B_{12}^+ + B_{12}^- = \Sigma B_1 + \Sigma B_{12}, \tag{3-5}$$

where the quantity on the right-hand side is the sum of the exterior entropy impulses B_1 received from outside the system and the entropy impulses B_{12} received from ball $\mathscr{B}_2$.

By means of relationship (3-2), the second law of thermodynamics gives

$$[\mathscr{E}_1] - \overline{T}_1[\mathscr{S}_1] \leq [T_1](\Delta B_1 + \Delta B_{12}) + A_1[\beta_1],$$

or, by introducing the free energy $\Psi = \mathscr{E} - T\mathscr{S}$,

$$[\Psi_1] + \overline{\mathscr{S}}_1[T_1] \leq [T_1](\Delta B_1 + \Delta B_{12}) + A_1[\beta_1]. \tag{3-6}$$

The free energy of ball $\mathscr{B}_1$ is

$$\Psi_1(T_1, \beta_1) = -C_1 T_1 \log T_1 - \beta_1 \frac{L}{T_0}(T_1 - T_0) + I(\beta_1),$$

where C_1 is the heat capacity, L is the latent heat at the phase change temperature T_0, and I is the indicator function of the interval [0, 1] (see [Moreau 1966–1967]), which takes into account the internal constraint on the volume fraction $0 \leq \beta_1 \leq 1$. We set

$$\widehat{\Psi}_1(T_1, \beta_1) = -\beta_1 \frac{L}{T_0}(T_1 - T_0) + I(\beta_1).$$

Then

$$[\Psi_1] = [-C_1 T_1 \log T_1] + [\widehat{\Psi}_1], \tag{3-7}$$

where

$$[\widehat{\Psi}_1] = \widehat{\Psi}_1(T_1^+, \beta_1^+) - \widehat{\Psi}_1(T_1^-, \beta_1^-) = \widehat{\Psi}_1(T_1^+, \beta_1^+) - \widehat{\Psi}_1(T_1^+, \beta_1^-) + \widehat{\Psi}_1(T_1^+, \beta_1^-) - \widehat{\Psi}_1(T_1^-, \beta_1^-) \tag{3-8}$$

and

$$\widehat{\Psi}_1(T_1^+, \beta_1^-) - \widehat{\Psi}_1(T_1^-, \beta_1^-) = -\beta_1^- \frac{L}{T_0}[T_1]. \tag{3-9}$$

In view of (3-7)–(3-9), inequality (3-6) transforms into

$$\begin{aligned}[\Psi_1] + \overline{\mathscr{S}}_1[T_1] &= [-C_1 T_1 \log T_1] + \widehat{\Psi}_1(T_1^+, \beta_1^+) - \widehat{\Psi}_1(T_1^+, \beta_1^-) - \beta_1^- \frac{L}{T_0}[T_1] + \overline{\mathscr{S}}_1[T_1] \\ &\leq [T_1](\Delta B_1 + \Delta B_{12}) + A_1[\beta_1].\end{aligned} \tag{3-10}$$

Since

$$\frac{[-C_1 T_1 \log T_1]}{[T_1]}$$

has a limit when $[T_1] \to 0$, we introduce the notation

$$[-C_1 T_1 \log T_1] + \Big(\overline{\mathscr{S}}_1 - \beta_1^- \frac{L}{T_0}\Big)[T_1] = -\mathscr{S}_1[T_1]. \tag{3-11}$$

From (3-10), we have

$$\widehat{\Psi}_1(T_1^+, \beta_1^+) - \widehat{\Psi}_1(T_1^+, \beta_1^-) \le [T_1](\Delta B_1 + \Delta B_{12} + \mathscr{S}_1) + A_1[\beta_1]. \tag{3-12}$$

It is reasonable to assume that there is no dissipation with respect to $[T_1]$ as there is no dissipation with respect to dT_1/dt in a smooth evolution

$$\Delta B_1 + \Delta B_{12} + \mathscr{S}_1 = 0; \tag{3-13}$$

then, inequality (3-12) becomes

$$\widehat{\Psi}_1(T_1^+, \beta_1^+) - \widehat{\Psi}_1(T_1^+, \beta_1^-) \le A_1[\beta_1]. \tag{3-14}$$

Turning now to the system as a whole, its entropy is given by the sum

$$\mathscr{S} = \mathscr{S}_1 + \mathscr{S}_2 + \mathscr{S}^{\text{int}}, \tag{3-15}$$

where $\mathscr{S}^{\text{int}}$ is the interaction entropy. The second law of thermodynamics is

$$[\mathscr{S}] = [\mathscr{S}_1] + [\mathscr{S}_2] + [\mathscr{S}^{\text{int}}] \ge B_1^+ + B_1^- + B_2^+ + B_2^- = \Sigma B_1 + \Sigma B_2. \tag{3-16}$$

In the sequel, we choose constitutive laws such that laws of thermodynamics (3-5) and (3-16) are satisfied. They will be such that (3-5) and

$$[\mathscr{S}^{\text{int}}] \ge -\Sigma B_{12} - \Sigma B_{21} \tag{3-17}$$

are verified.

Let us get inequalities equivalent to (3-17). Let

$$\Theta = \frac{T_1 + T_2}{2}.$$

From (3-4) and (3-17), we have

$$\begin{aligned}[\mathscr{E}^{\text{int}}] - \overline{\Theta}[\mathscr{S}^{\text{int}}] \le P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - \overline{T}_1 \Sigma B_{12} - [T_1]\Delta B_{12}& \\ - \overline{T}_2 \Sigma B_{21} - [T_2]\Delta B_{21} + \overline{\Theta}(\Sigma B_{12} + \Sigma B_{21}).& \end{aligned} \tag{3-18}$$

Introducing the free energy of interaction $\Psi^{\text{int}} = \mathscr{E}^{\text{int}} - \Theta\mathscr{S}^{\text{int}}$, inequality (3-18) can be written as

$$\begin{aligned}[\Psi^{\text{int}}] + \overline{\mathscr{S}}^{\text{int}}[\Theta] \le P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - \overline{T}_1 \Sigma B_{12} - [T_1]\Delta B_{12}& \\ - \overline{T}_2 \Sigma B_{21} - [T_2]\Delta B_{21} + \overline{\Theta}(\Sigma B_{12} + \Sigma B_{21}),& \end{aligned} \tag{3-19}$$

where

$$\overline{\mathscr{S}}^{\text{int}} = \frac{(\mathscr{S}^{\text{int}})^+ + (\mathscr{S}^{\text{int}})^-}{2}, \qquad [\Theta] = \frac{[T_1] + [T_2]}{2}.$$

We assume Ψ^{int} is a smooth function of Θ. Then when $[\Theta]$ tends to 0 and Θ^+ and Θ^- have limits

$$\lim_{[\Theta]\to 0} \Theta^+ = \lim_{[\Theta]\to 0} \Theta^- = \Theta,$$

we have

$$\lim_{[\Theta]\to 0}\left(\frac{[\Psi^{\text{ int}}]}{[\Theta]} + \overline{\mathcal{S}}^{\text{int}}\right) = 0,$$

since

$$\lim_{[\Theta]\to 0} \frac{[\Psi^{\text{int}}]}{[\Theta]} = \frac{\partial \Psi^{\text{int}}}{\partial \Theta}(\Theta), \qquad \lim_{[\Theta]\to 0} \overline{\mathcal{S}}^{\text{int}} = \mathcal{S}^{\text{int}}(\Theta),$$

and the Helmholtz relationship

$$\mathcal{S}^{\text{int}}(\Theta) = -\frac{\partial \Psi^{\text{int}}}{\partial \Theta}(\Theta).$$

Therefore, we can put

$$[\Psi^{\text{int}}] + \overline{\mathcal{S}}^{\text{int}}[\Theta] = -\mathcal{S}^{\text{int}}[\Theta], \tag{3-20}$$

and, from (3-19), we find

$$0 \le P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - \overline{T}_1 \Sigma B_{12} - [T_1]\Big(\Delta B_{12} - \frac{\mathcal{S}^{\text{int}}}{2}\Big) - \overline{T}_2 \Sigma B_{21} - [T_2]\Big(\Delta B_{21} - \frac{\mathcal{S}^{\text{int}}}{2}\Big) + \overline{\Theta}(\Sigma B_{12} + \Sigma B_{21}). \tag{3-21}$$

It is reasonable to assume that there is no dissipation with respect to $[T_1]$ and $[T_2]$ as there is no dissipation with respect to the dT/dt's in a smooth evolution

$$\Delta B_{12} - \frac{\mathcal{S}^{\text{int}}}{2} = 0, \qquad \Delta B_{21} - \frac{\mathcal{S}^{\text{int}}}{2} = 0; \tag{3-22}$$

then

$$0 \le P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - \overline{T}_1 \Sigma B_{12} - \overline{T}_2 \Sigma B_{21} + \overline{\Theta}(\Sigma B_{12} + \Sigma B_{21}). \tag{3-23}$$

But

$$\overline{T}_1 \Sigma B_{12} + \overline{T}_2 \Sigma B_{21} = \overline{\Theta}(\Sigma B_{12} + \Sigma B_{21}) + \delta\overline{T}\,\frac{\Sigma B_{21} - \Sigma B_{12}}{2}, \tag{3-24}$$

where the difference in temperature, $\delta\overline{T}$, is defined by $\delta\overline{T} = \overline{T}_2 - \overline{T}_1$. Finally, inequality (3-23) yields

$$0 \le P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - \delta\overline{T}\,\frac{\Sigma B_{21} - \Sigma B_{12}}{2}; \tag{3-25}$$

this last relationship links mechanical and thermal dissipations.

On the other hand, from (3-25), by means of (3-24) and assuming no dissipation with respect to $[T_1]$ and $[T_2]$, it follows that (3-21) is satisfied; thanks to (3-20), inequality (3-21) yields

$$[\Psi^{\text{int}}] \le P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - \overline{T}_1 \Sigma B_{12} - [T_1]\Delta B_{12} - \overline{T}_2 \Sigma B_{21} - [T_2]\Delta B_{21} + \overline{\Theta}(\Sigma B_{12} + \Sigma B_{21}) - \overline{\mathcal{S}}^{\text{int}}[\Theta]. \tag{3-26}$$

Substituting the identity $[\Psi^{\text{int}}] = [\mathscr{E}^{\text{int}}] - [\Theta]\overline{\mathscr{S}}^{\text{int}} - \overline{\Theta}[\mathscr{S}^{\text{int}}]$ into (3-26), we have

$$\begin{aligned} -\overline{\Theta}[\mathscr{S}^{\text{int}}] \le -[\mathscr{E}^{\text{int}}] + P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - \overline{T}_1 \Sigma B_{12} - [T_1]\Delta B_{12} \\ - \overline{T}_2 \Sigma B_{21} - [T_2]\Delta B_{21} + \overline{\Theta}(\Sigma B_{12} + \Sigma B_{21}); \end{aligned} \tag{3-27}$$

this in turn, by virtue of (3-4), entails $-\overline{\Theta}[\mathscr{S}^{\text{int}}] \le \overline{\Theta}(\Sigma B_{12} + \Sigma B_{21})$, which is inequality (3-17).

As a consequence, the following theorem holds.

Theorem 3.1. *Let Ψ^{int} be a smooth function of Θ. We assume (3-22) holds, that is, there is no dissipation with respect to $[T_1]$ and $[T_2]$. If (3-4) is satisfied, then (3-17) and (3-25) are equivalent.*

4. The constitutive laws

For ball $\mathscr{B}_1$, we split the interior force A_1 into a possibly nondissipative part, indexed by $^{\text{nd}}$, and a dissipative part, indexed by $^{\text{d}}$:

$$A_1 = A_1^{\text{nd}} + A_1^{\text{d}}. \tag{4-1}$$

The interior force A_1^{nd} is defined by the free energy $\Psi_1(T_1, \beta_1)$ as

$$A_1^{\text{nd}} \in \partial\Psi_1(T_1^+, \beta_1^+) = -\frac{L}{T_0}(T_1^+ - T_0) + A_1^{\text{ndr}}, \tag{4-2}$$

where the subdifferential $\partial\Psi_1$ [Moreau 1966–1967] is computed with respect to β_1^+ and the reaction A_1^{ndr} is such that

$$A_1^{\text{ndr}} \in \partial I(\beta_1^+). \tag{4-3}$$

The dissipative interior force A_1^{d} is defined by

$$A_1^{\text{d}} \in \partial\Phi_1([\beta_1]), \tag{4-4}$$

and satisfies

$$A_1^{\text{d}}[\beta_1] \ge 0, \tag{4-5}$$

where $\Phi_1([\beta_1])$ is a pseudopotential of dissipation [Moreau 1970] and the subdifferential is computed with respect to $[\beta_1]$.

For the system, we choose the pseudopotential of dissipation

$$\Phi\bigg(D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big), \delta\overline{T}, \chi\bigg),$$

which depends on the velocity $D\big((\boldsymbol{U}^+ + \boldsymbol{U}^-)/2\big)$, on the thermal heterogeneity $\delta\overline{T}$, and on the quantity $\chi = D(\boldsymbol{U}^-/2)$ depending on the past, to ensure the noninterpenetration of the two balls [Frémond 2001; 2007].

The constitutive laws are relationships (4-2)–(4-5) and

$$\Big(P^{\text{int}}, \frac{\Sigma B_{21} - \Sigma B_{12}}{2}\Big) \in \partial\Phi\bigg(D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big), \delta\overline{T}, \chi\bigg), \tag{4-6}$$

where the subdifferential set of Φ is computed with respect to the first two variables.

Remark 4.1. The reaction to the internal constraint $0 \le \beta^+ \le 1$ is in general dissipative, because $\partial I(\beta^+)(\beta^+ - \beta^-)$ may be different from zero — in fact, positive. Thus, the reaction is dissipative, as we may expect. This property is not true in a smooth evolution where the internal constraint is workless or nondissipative, because

$$\partial I(\beta)\frac{\mathrm{d}\beta}{\mathrm{d}t} = 0, \quad \text{almost everywhere.}$$

Remark 4.2. From (4-6), applying the classical properties of pseudopotentials [Moreau 1970] we see that inequality (3-25) is satisfied.

Theorem 4.3. *If the constitutive laws* (4-2) *and* (4-4) *are satisfied, then inequality* (3-14) *holds and the internal constraint* $0 \le \beta_1^+ \le 1$ *is verified.*

Proof. If $A_1^{\mathrm{nd}} \in \partial\Psi_1(T_1^+, \beta_1^+)$, then, using the definition of subdifferential, we have

$$\widehat{\Psi}_1(T_1^+, \beta_1^+) - \widehat{\Psi}_1(T_1^+, \beta_1^-) \le A_1^{\mathrm{nd}}(\beta_1^+ - \beta_1^-) = A_1^{\mathrm{nd}}[\beta_1];$$

with (4-5), resulting from (4-4), the previous inequality entails

$$\widehat{\Psi}_1(T_1^+, \beta_1^+) - \widehat{\Psi}_1(T_1^+, \beta_1^-) \le A_1^{\mathrm{nd}}[\beta_1] + A_1^{\mathrm{d}}[\beta_1] = A_1[\beta_1].$$

Since $\partial\Psi_1(T_1^+, \beta_1^+) \ne \varnothing$, the internal constraint $0 \le \beta_1^+ \le 1$ is verified. □

Theorem 4.4. *Assume* (3-13) *and* (3-22) *hold, that is, there is no dissipation with respect to* $[T_1]$ *and* $[T_2]$. *If the first laws of thermodynamics* (3-2) *and* (3-3) *and the constitutive laws* (4-2), (4-3), (4-4) *and* (4-6) *are verified, then the second law of thermodynamics holds for each ball and for the system.*

Proof. Due to Theorem 4.3 and relationships (3-7)–(3-9), we find

$$\begin{aligned}[\Psi_1] &= [-C_1 T_1 \log T_1] + \widehat{\Psi}_1(T_1^+, \beta_1^+) - \widehat{\Psi}_1(T_1^+, \beta_1^-) - \beta_1^- \frac{L}{T_0}[T_1] \\ &\le [-C_1 T_1 \log T_1] + A_1[\beta_1] - \beta_1^- \frac{L}{T_0}[T_1].\end{aligned} \tag{4-7}$$

On the other hand, we have

$$[\Psi_1] = [\mathscr{E}_1] - [T_1 \mathscr{S}_1] = [\mathscr{E}_1] - [T_1]\overline{\mathscr{S}}_1 - \overline{T}_1[\mathscr{S}_1]. \tag{4-8}$$

From (3-2), (4-7) and (4-8), it follows that

$$\begin{aligned}\overline{T}_1[\mathscr{S}_1] &\ge [\mathscr{E}_1] - [T_1]\overline{\mathscr{S}}_1 + [C_1 T_1 \log T_1] - A_1[\beta_1] + \beta_1^- \frac{L}{T_0}[T_1] \\ &= \overline{T}_1(\Sigma B_1 + \Sigma B_{12}) + [T_1](\Delta B_1 + \Delta B_{12}) + A_1[\beta_1] - [T_1]\overline{\mathscr{S}}_1 \\ &\qquad + [C_1 T_1 \log T_1] - A_1[\beta_1] + \beta_1^- \frac{L}{T_0}[T_1] \\ &= \overline{T}_1(\Sigma B_1 + \Sigma B_{12}) + [T_1](\Delta B_1 + \Delta B_{12} + \mathscr{S}_1),\end{aligned}$$

with $\mathscr{S}_1$ defined as in (3-11). From the previous inequality, assuming no dissipation with respect to $[T_1]$ (relationship (3-13)), we obtain

$$[\mathscr{S}_1] \ge \Sigma B_1 + \Sigma B_{12}, \tag{4-9}$$

that is, the second law of thermodynamics for ball $\mathscr{B}_1$.

It is worth noting that, if (4-9) holds for each ball, then, in view of (3-15) and (3-17), we have

$$[\mathcal{S}] = [\mathcal{S}_1] + [\mathcal{S}_2] + [\mathcal{S}^{\text{int}}] \geq \Sigma B_1 + \Sigma B_{12} + \Sigma B_2 + \Sigma B_{21} - \Sigma B_{12} - \Sigma B_{21} = \Sigma B_1 + \Sigma B_2,$$

which is the second law of thermodynamics for the system. Therefore, all that is necessary is proving that our hypotheses imply (3-17). Due to the constitutive law (4-6), inequality (3-25) is satisfied, and, from Theorem 3.1, our conclusion follows. □

5. Examples of thermal effects with phase changes

We choose a pseudopotential of dissipation, Φ, without nondiagonal terms, for example

$$\Phi\left(D\left(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\right), \delta\overline{T}, D\left(\frac{\boldsymbol{U}^-}{2}\right)\right) = \Phi^{\text{mech}}\left(D\left(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\right), D\left(\frac{\boldsymbol{U}^-}{2}\right)\right) + \frac{\lambda}{4}(\delta\overline{T})^2;$$

with this choice, the mechanical problem is split from the thermal one. The thermal constitutive law is

$$\Sigma B_{21} - \Sigma B_{12} = -\lambda\delta\overline{T}. \tag{5-1}$$

Let us recall that the free energies chosen for the balls are

$$\Psi_i(T_i, \beta_i) = -C_i T_i \log T_i - \beta_i \frac{L}{T_0}(T_i - T_0) + I(\beta_i), \qquad i = 1, 2.$$

We choose the free energy of interaction $\Psi^{\text{int}} = 0$; we have $\mathcal{S}^{\text{int}} = 0$ and, from relationships (3-22), $\Delta B_{12} = 0$, $\Delta B_{21} = 0$.

Now, we suppose that the macroscopic mechanical problem is solved, that is, we know the quantity $P^{\text{int}} D(\boldsymbol{U}^+ + \boldsymbol{U}^-)/2$ and we assume no external percussion work $A_1 = A_2 = 0$, due to the equations of motion (2-2); the thermal equations are

$$[\mathcal{S}_1] = [C_1 \log T_1] + \frac{L}{T_0}[\beta_1] = C_1 \log \frac{T_1^+}{T_1^-} + \frac{L}{T_0}[\beta_1] = \Sigma B_1 + \Sigma B_{12},$$

$$[\mathcal{S}_2] = [C_2 \log T_2] + \frac{L}{T_0}[\beta_2] = C_2 \log \frac{T_2^+}{T_2^-} + \frac{L}{T_0}[\beta_2] = \Sigma B_2 + \Sigma B_{21},$$

$$[\mathcal{E}_1] = C_1[T_1] + L[\beta_1] = \overline{T}_1(\Sigma B_1 + \Sigma B_{12}) + [T_1]\Delta B_1,$$

$$[\mathcal{E}_2] = C_2[T_2] + L[\beta_2] = \overline{T}_2(\Sigma B_2 + \Sigma B_{21}) + [T_2]\Delta B_2,$$

$$[\mathcal{E}^{\text{int}}] = P^{\text{int}} D\left(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\right) - \overline{T}_1 \Sigma B_{12} - \overline{T}_2 \Sigma B_{21} = 0,$$

where the mechanical dissipation $P^{\text{int}} D\big((\boldsymbol{U}^+ + \boldsymbol{U}^-)/2\big)$ is positive due to the properties of pseudopotentials of dissipation. These equations are completed by the description of thermal relationships between the system and the outside and by the equations of microscopic motion

$$0 = A_i = A_i^{\text{nd}} + A_i^{\text{d}} \in -\frac{L}{T_0}(T_i^+ - T_0) + \partial I(\beta_i^+) + \partial\Phi_i([\beta_i]), \qquad i = 1, 2.$$

We assume the collision is adiabatic, that is, no heat is exchanged with the exterior:

$$T_1^+ B_1^+ + T_1^- B_1^- = \overline{T}_1 \Sigma B_1 + [T_1] \Delta B_1 = 0,$$
$$T_2^+ B_2^+ + T_2^- B_2^- = \overline{T}_2 \Sigma B_2 + [T_2] \Delta B_2 = 0,$$

and we have the equations

$$[\mathcal{S}_1] = C_1 \log \frac{T_1^+}{T_1^-} + \frac{L}{T_0}[\beta_1] = \Sigma B_1 + \Sigma B_{12},$$
$$[\mathcal{S}_2] = C_2 \log \frac{T_2^+}{T_2^-} + \frac{L}{T_0}[\beta_2] = \Sigma B_2 + \Sigma B_{21},$$
$$C_1[T_1] + L[\beta_1] = \overline{T}_1 \Sigma B_{12}, \qquad C_2[T_2] + L[\beta_2] = \overline{T}_2 \Sigma B_{21},$$
$$P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) = C_1[T_1] + L[\beta_1] + C_2[T_2] + L[\beta_2], \tag{5-2}$$
$$C_2 \frac{[T_2]}{\overline{T}_2} + \frac{L}{\overline{T}_2}[\beta_2] - C_1 \frac{[T_1]}{\overline{T}_1} - \frac{L}{\overline{T}_1}[\beta_1] = -\lambda \delta \overline{T}. \tag{5-3}$$

The last two equations give the temperatures T_1^+ and T_2^+ after the collision, and the first give the entropic heat exchanges, ΣB_1 and ΣB_2, with the outside.

We assume also small perturbations, that is $T_i^\pm = T_0 + \theta_i^\pm$, $|\theta_i^\pm| \ll T_0$. We can write (5-2) and (5-3) as

$$P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) = C_1[\theta_1] + L[\beta_1] + C_2[\theta_2] + L[\beta_2], \tag{5-4}$$
$$C_2 \frac{[\theta_2]}{T_0} + \frac{L}{T_0}[\beta_2] - C_1 \frac{[\theta_1]}{T_0} - \frac{L}{T_0}[\beta_1] = -\lambda \Big(\theta_2^- - \theta_1^- + \frac{[\theta_2]}{2} - \frac{[\theta_1]}{2}\Big), \tag{5-5}$$

and we get the system

$$C_1[\theta_1] = \frac{1}{2}\bigg(P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - 2L[\beta_1] + \lambda T_0 \Big(\theta_2^- - \theta_1^- + \frac{[\theta_2]}{2} - \frac{[\theta_1]}{2}\Big)\bigg), \tag{5-6}$$
$$C_2[\theta_2] = \frac{1}{2}\bigg(P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - 2L[\beta_2] - \lambda T_0 \Big(\theta_2^- - \theta_1^- + \frac{[\theta_2]}{2} - \frac{[\theta_1]}{2}\Big)\bigg), \tag{5-7}$$

where the volume fractions β_1 and β_2 satisfy the equations of microscopic motion

$$0 \in -\frac{L}{T_0}(T_1^+ - T_0) + \partial I(\beta_1^+) + \partial \Phi_1([\beta_1]), \tag{5-8}$$
$$0 \in -\frac{L}{T_0}(T_2^+ - T_0) + \partial I(\beta_2^+) + \partial \Phi_2([\beta_2]), \tag{5-9}$$

which are equivalent to

$$\theta_1^+ \in \partial I(\beta_1^+) + \frac{T_0}{L} \partial \Phi_1([\beta_1]), \tag{5-10}$$
$$\theta_2^+ \in \partial I(\beta_2^+) + \frac{T_0}{L} \partial \Phi_2([\beta_2]). \tag{5-11}$$

It is easy to prove that Equations (5-6), (5-10), and (5-7), (5-11), giving the temperatures and phase fractions θ_1^+, θ_2^+ and β_1^+, β_2^+, have unique solutions.

5.1. ***Collision of two pieces of ice at the same temperature.*** The temperatures after the collision are equal. Equations (5-6) and (5-10) show that they do not depend on λ.

We consider two identical balls of ice, $C_1 = C_2 = C$, at the same temperature, θ^-, before the collision. The balls have the same temperature and volume fraction, denoted by θ^+ and β^+, after the collision:

$$\begin{aligned} \theta_1^- &= \theta_2^- = \theta^-, & \theta_1^+ &= \theta_2^+ = \theta^+, \\ \beta_1^- &= \beta_2^- = 0, & \beta_1^+ &= \beta_2^+ = \beta^+. \end{aligned} \tag{5-12}$$

We know that the smooth ice-water phase change is not dissipative. Thus we assume we're not in a nonsmooth situation; there is no dissipation with respect to the volume fractions' discontinuities $[\beta_1]$ and $[\beta_2]$:

$$\Phi_1([\beta_1]) = \Phi_2([\beta_2]) = 0. \tag{5-13}$$

Equations (5-6) and (5-7) give

$$C[\theta] = \tfrac{1}{2}(\mathcal{T} - 2L\beta^+), \tag{5-14}$$

where

$$\mathcal{T} = P^{\mathrm{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) \geq 0.$$

Because of (5-13), we find easily from the equations of microscopic motion (5-10) and (5-11)

$$\theta^+ \in \partial I(\beta^+). \tag{5-15}$$

Theorem 5.1. (1) *If $\mathcal{T} \leq -2C\theta^-$, then $\beta^+ = 0$: the ice does not melt and has temperature* (5-14) *after collision.*

(2) *If $\mathcal{T} \geq 2(L - C\theta^-)$, then $\beta^+ = 1$: the ice melts. The liquid water has temperature* (5-14) *after collision.*

(3) *If $-2C\theta^- < \mathcal{T} < 2(L - C\theta^-)$, then $0 < \beta^+ < 1$: after collision there is a mixture of ice and liquid water with temperature $\theta^+ = 0$.*

Proof. (1) If $\mathcal{T} \leq -2C\theta^-$, then, from (5-14), it follows that $C[\theta] + L\beta^+ \leq -C\theta^-$. The previous inequality entails

$$\theta^+ \leq -\frac{L}{C}\beta^+ \leq 0;$$

therefore, in view of (5-15), we obtain $\beta^+ = 0$.

Cases (2) and (3) are easily proved. □

The results of the theorem agree with what is expected: A violent collision produces a phase change whereas a nonviolent collision does not. Violent means dissipative, that is, $\mathcal{T}$ large.

Remark 5.2. In the case where the phase change, for another material, is dissipative, we choose the pseudopotential of dissipation as

$$\Phi_i([\beta_i]) = \frac{c}{2}[\beta_i]^2, \qquad i = 1, 2,$$

where c is a positive constant. Thus, the equations of motion (5-8) give

$$\frac{L}{T_0}\theta_1^+ \in \partial I(\beta_1^+) + c[\beta_1], \qquad \frac{L}{T_0}\theta_2^+ \in \partial I(\beta_2^+) + c[\beta_2],$$

and we have the equations

$$C[\theta] = \tfrac{1}{2}(\mathcal{T} - 2L\beta^+), \qquad \frac{L}{T_0}\theta^+ \in \partial I(\beta^+) + c\beta^+.$$

The following result is easily proved, assuming (5-12) before collision.

Theorem 5.3. (1) *If $\mathcal{T} \le -2C\theta^-$, then $\beta^+ = 0$ and there is solid with $\theta^+ < cT_0/L$.*

(2) *If $\mathcal{T} \ge 2(L - C\theta^- + cCT_0/L)$, then $\beta^+ = 1$ and there is liquid with $\theta^+ \ge cT_0/L$.*

(3) *If $-2C\theta^- < \mathcal{T} < 2(L - C\theta^- + cCT_0/L)$, then $0 < \beta^+ < 1$ and there is a mixture of solid and liquid with $\theta^+ = cT_0\beta^+/L$.*

When there is dissipation the collision has to be more violent to melt the solid balls. The phase change occurs with temperature slightly above T_0, as is the case for dissipative phase changes [Frémond and Visintin 1985; Frémond 2001; 2005].

5.2. ***Collision of two pieces of ice at different temperatures.*** When two pieces of ice at different temperatures collide, the dissipation due to the collision may be large enough to melt the warmest of them. We look for conditions on the state quantities before the collision and on the dissipated work, such that this phenomenon occurs. We expect that the temperatures before collision cannot be very cold and that the dissipated work has to be large.

We assume that there is no dissipation with respect to $[\beta_1]$ and $[\beta_2]$, that is,

$$\Phi_1([\beta_1]) = \Phi_2([\beta_2]) = 0,$$

and thus the equations of microscopic motion are, from (5-10) and (5-11),

$$\theta_1^+ \in \partial I(\beta_1^+), \qquad \theta_2^+ \in \partial I(\beta_1^+). \tag{5-16}$$

The two identical pieces of ice before collision satisfy $\beta_1^- = \beta_2^- = 0$, $\theta_1^- \le 0$, $\theta_2^- \le 0$. We look for conditions such that ball 1 melts and ball 2 remains frozen:

$$\beta_1^+ = 1, \qquad \beta_2^+ = 0. \tag{5-17}$$

Thus from (5-16), we have

$$\theta_1^+ \ge 0, \qquad \theta_2^+ \le 0. \tag{5-18}$$

The values of λ and C depend on the relative importances of the volumes and surface areas of the pieces of ice. We study the two cases, when λ is either small or large with respect to C (see Remark 5.4).

Suppose λ is small with respect to C/T_0. Equations (3-1) and (3-12) give

$$P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) = C_1[\theta_1] + L[\beta_1] + C_2[\theta_2] + L[\beta_2],$$
$$\Big(\frac{C_2}{T_0} + \frac{\lambda}{2}\Big)[\theta_2] + \frac{L}{T_0}[\beta_2] - \Big(\frac{C_1}{T_0} + \frac{\lambda}{2}\Big)[\theta_1] - \frac{L}{T_0}[\beta_1] = -\lambda(\theta_2^- - \theta_1^-).$$

We suppose λ to be small with respect to C_i/T_0, $i = 1, 2$ and we get

$$P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) = C_1[\theta_1] + L[\beta_1] + C_2[\theta_2] + L[\beta_2],$$
$$\frac{C_2}{T_0}[\theta_2] + \frac{L}{T_0}[\beta_2] - \frac{C_1}{T_0}[\theta_1] - \frac{L}{T_0}[\beta_1] = -\lambda(\theta_2^- - \theta_1^-),$$

which gives the system

$$\begin{aligned} C_1[\theta_1] &= \frac{1}{2}\Big(P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - 2L[\beta_1] + \lambda T_0(\theta_2^- - \theta_1^-)\Big), \\ C_2[\theta_2] &= \frac{1}{2}\Big(P^{\text{int}} D\Big(\frac{\boldsymbol{U}^+ + \boldsymbol{U}^-}{2}\Big) - 2L[\beta_2] - \lambda T_0(\theta_2^- - \theta_1^-)\Big), \end{aligned} \tag{5-19}$$

where the volume fractions β_1 and β_2 satisfy the equations of microscopic motion (5-16).

Equations (5-19) give with $C_1 = C_2 = C$, and (5-17)

$$C[\theta_1] = \tfrac{1}{2}\big(\mathcal{T} - 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big), \qquad C[\theta_2] = \tfrac{1}{2}\big(\mathcal{T} - \lambda T_0(\theta_2^- - \theta_1^-)\big). \tag{5-20}$$

By means of (5-20), conditions (5-18) are satisfied if and only if

$$(2C - \lambda T_0)\theta_1^- + \lambda T_0 \theta_2^- + \mathcal{T} - 2L \geq 0, \tag{5-21}$$
$$\lambda T_0 \theta_1^- + (2C - \lambda T_0)\theta_2^- + \mathcal{T} \leq 0, \tag{5-22}$$

with $\theta_1^- \leq 0$ and $\theta_2^- \leq 0$. Because of our hypothesis on λ, we have

$$2C - \lambda T_0 > 0. \tag{5-23}$$

- If $\mathcal{T} < 2L$, inequalities (5-21) and (5-23) show that it is impossible to satisfy system (5-21), (5-22) with $\theta_1^- \leq 0$ and $\theta_2^- \leq 0$. Thus, if the dissipation is small, it is impossible to melt one piece of ice. Both remain frozen.
- If $\mathcal{T} \geq 2L$, it is possible to find temperatures (θ_1^-, θ_2^-) satisfying the system (5-21), (5-22) with $\theta_1^- \leq 0$, $\theta_1^- \approx 0$ ($\theta_1^- = 0$ if $\mathcal{T} = 2L$), and $\theta_2^- < \theta_1^-$. Thus, if the dissipation is large, one piece of ice melts, and the other one remains frozen. The temperature of the coldest piece of ice has to be sufficiently cold.

Examples are given in Figures 1 and 2 for $\lambda = 0$ and $\lambda = 100$, $\mathcal{T} = 10L$, with $L = 3.33 \times 10^5$, $C = 10^6$, and $T_0 = 273$.

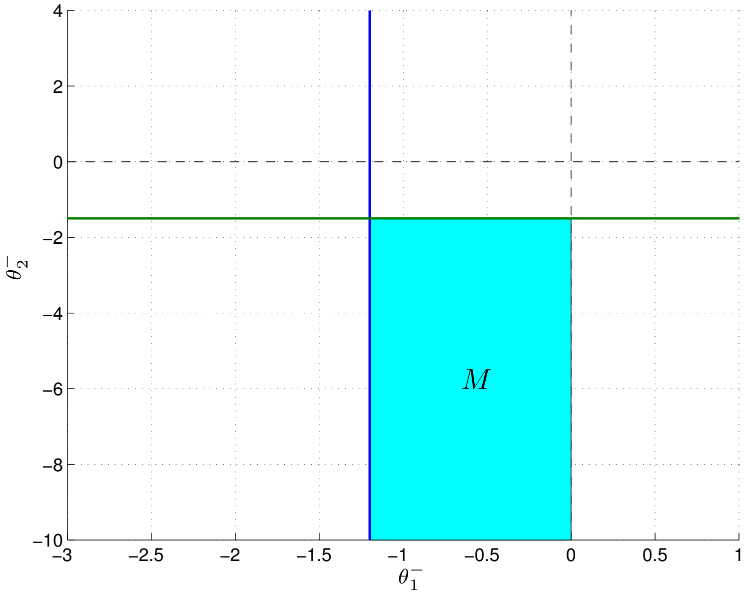

Figure 1. The case $\lambda = 0$ and $\mathcal{T} = 10L$ with $L = 3.33 \times 10^5$ and $C = 10^6$. The inequalities (5-21) and (5-22) have solutions if θ_1^- is negative and satisfies $\theta_1^- \geq -(\mathcal{T} - 2L)/2C$, equality on the blue line, and $\theta_2^- \leq -\mathcal{T}/2C$, equality on the green line. The point (θ_1^-, θ_2^-) has to belong to the set M.

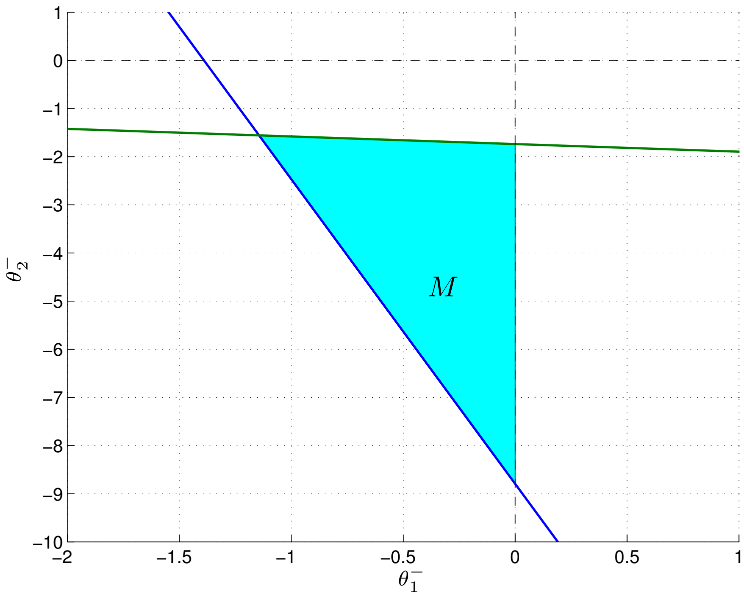

Figure 2. The case $\lambda = 1000$ and $\mathcal{T} = 10L$ with $L = 3.33 \times 10^5$ and $C = 10^6$. The inequalities (5-21) and (5-22) have solutions if point (θ_1^-, θ_2^-) belongs to the set M which is defined by the blue and green lines of (5-21), (5-22), and $\theta_1^- \leq 0$, $\theta_2^- \leq 0$.

Now suppose instead that λ is not small with respect to C/T_0. We have $[\beta_1]=1$ and $[\beta_2]=0$, and (5-4) and (5-5) give

$$\mathcal{T}=C[\theta_1]+L+C[\theta_2], \tag{5-24}$$

$$C\frac{[\theta_2]}{T_0}-C\frac{[\theta_1]}{T_0}-\frac{L}{T_0}=-\lambda\Big(\theta_2^- -\theta_1^- +\frac{[\theta_2]}{2}-\frac{[\theta_1]}{2}\Big). \tag{5-25}$$

From (5-24), we get

$$[\theta_2]=\frac{1}{C}\big(\mathcal{T}-C[\theta_1]-L\big); \tag{5-26}$$

substituting (5-26) into (5-25), we obtain

$$\begin{aligned}\theta_1^+&=\frac{2C}{2C+\lambda T_0}\theta_1^- +\frac{\lambda T_0}{2C+\lambda T_0}\theta_2^- +\frac{\mathcal{T}-L}{2C}-\frac{L}{2C+\lambda T_0},\\ \theta_2^+&=\frac{2C}{2C+\lambda T_0}\theta_2^- +\frac{\lambda T_0}{2C+\lambda T_0}\theta_1^- +\frac{\mathcal{T}-L}{2C}+\frac{L}{2C+\lambda T_0}.\end{aligned} \tag{5-27}$$

Conditions (5-18) are satisfied if and only if

$$\frac{2C}{2C+\lambda T_0}\theta_1^- +\frac{\lambda T_0}{2C+\lambda T_0}\theta_2^- +\frac{\mathcal{T}-L}{2C}-\frac{L}{2C+\lambda T_0}\geq 0, \tag{5-28}$$

$$\frac{2C}{2C+\lambda T_0}\theta_2^- +\frac{\lambda T_0}{2C+\lambda T_0}\theta_1^- +\frac{\mathcal{T}-L}{2C}+\frac{L}{2C+\lambda T_0}\leq 0. \tag{5-29}$$

Since $\theta_1^-\leq 0$ and $\theta_2^-\leq 0$, to satisfy (5-28) a necessary condition is

$$\frac{\mathcal{T}-L}{2C}\geq\frac{L}{2C+\lambda T_0}.$$

Thus the dissipation has to be large in order to melt one of the pieces of ice.

- If $\lambda<2C/T_0$, the system (5-28), (5-29) has solutions (θ_1^-,θ_2^-), θ_1^-, and $\theta_2^-\leq 0$, if

  $$\frac{\mathcal{T}-L}{2C}\geq\frac{L}{2C-\lambda T_0}>\frac{L}{2C+\lambda T_0};$$

  in agreement with the case λ negligible; see the left halves of Figures 3 and 4. If λ is small, only the mechanical effect warms the balls whereas the conduction has a negligible effect. We have $\theta_2^-\leq\theta_1^-\leq 0$ and $\theta_2^+\leq 0\leq\theta_1^+$. The warmest piece of ice melts in the collision and the coldest remains frozen.

- If $\lambda>2C/T_0$, the system (5-28), (5-29) has solutions θ_1^- and $\theta_2^-\leq 0$ if

  $$\frac{\mathcal{T}-L}{2C}\geq-\frac{L}{2C-\lambda T_0}>\frac{L}{2C+\lambda T_0},$$

  see the right halves of Figures 3 and 4. If C is small, that is, if the heat capacity is negligible, it is difficult for the system to store energy (the only possibility for storing energy is with a phase change). Since we have assumed the system to be adiabatic, the heat has to remain in the system and very large temperature variations occur: the effect of conduction is added to the mechanical effect and it

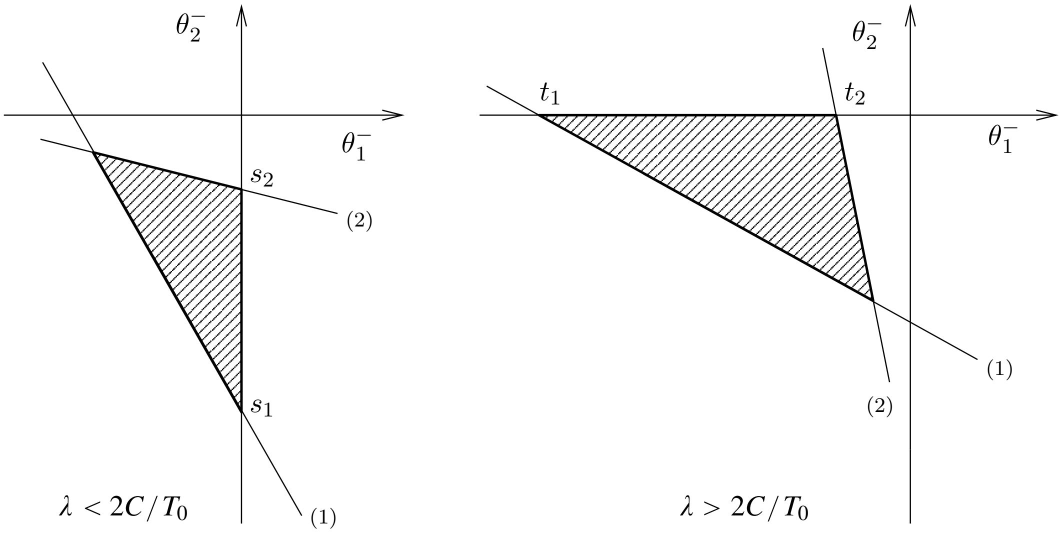

Figure 3. Condition (5-28), curve (1), and condition (5-29), curve (2). For ball 1 to be unfrozen after collision while ball 2 remains frozen, the temperatures θ_1^- and θ_2^- have to be in the hatched triangles.

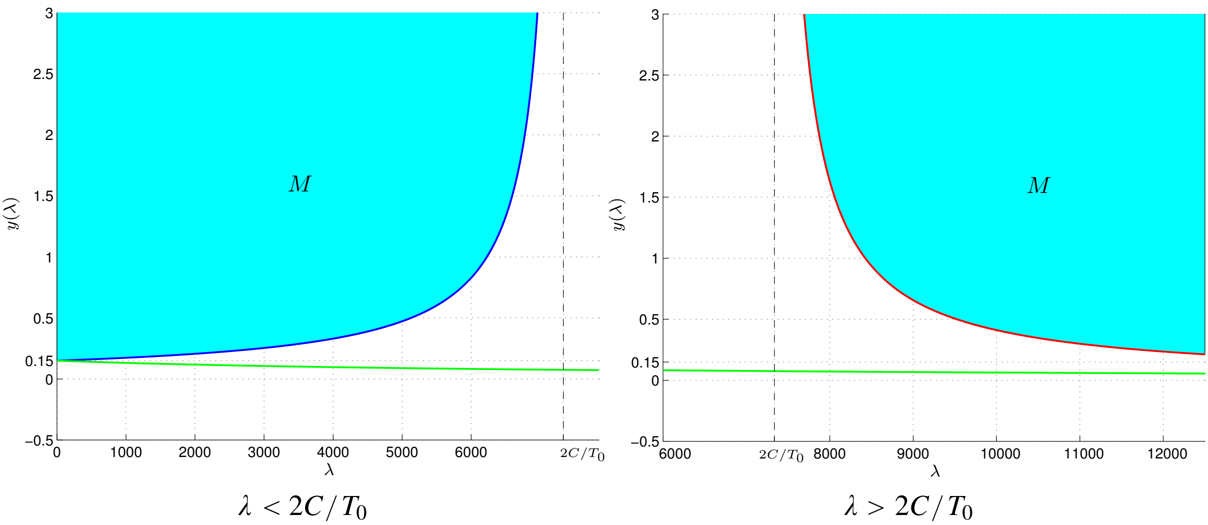

Figure 4. The curve $y_1(\lambda) = L/(2C - \lambda T_0)$ versus λ in blue, the curve $y_2(\lambda) = -y_1(\lambda)$ in red, and the curve $y_3(\lambda) = L/(2C + \lambda T_0)$ in green. The quantity $(\mathcal{T} - L)/2C$ has to be in the blue domain M for ball number 1 to melt. Thus the collision has to be violent enough, that is, $\mathcal{T}$ large enough, for ball number 1 to melt.

increases the temperature of the coldest ball. Therefore, the coldest ball before collision becomes the warmest and vice versa. We have $\theta_1^- \le \theta_2^- \le 0$ and $\theta_2^+ \le 0 \le \theta_1^+$. In the extreme situation where $\lambda = \infty$, formulae (5-27) show that $\theta_1^+ = \theta_2^-$ and $\theta_2^+ = \theta_1^-$. When the thermal dissipation is very large the temperatures exchange. Let us note that the same result holds for the velocities when the mechanical pseudopotential of dissipation,

$$\Phi^{\text{mech}}\left(D\left(\frac{\boldsymbol{U}^{+}+\boldsymbol{U}^{-}}{2}\right), D\left(\frac{\boldsymbol{U}^{-}}{2}\right)\right),$$

involves a quadratic potential

$$k\left(D\left(\frac{\boldsymbol{U}^{+}+\boldsymbol{U}^{-}}{2}\right)\right)^{2};$$

see for instance [Frémond 2001] or [Frémond 2007, page 51]. When the mechanical dissipation parameter $k=\infty$, the velocities exchange, $\boldsymbol{U}_1^{+}=\boldsymbol{U}_2^{-}$, $\boldsymbol{U}_2^{+}=\boldsymbol{U}_1^{-}$, if the two balls have same mass, see [Frémond 2001] or [Frémond 2007, page 53].

In the extreme situation where the heat capacity is zero, $C=0$, the system cannot store energy except by changing phase. The energy L which is needed to melt the piece of ice has to be equal to the dissipated work $\mathcal{T}$ and the discontinuities of temperature are opposite due to (5-24) extended by continuity.

- If $\lambda=2C/T_0$, then, from (5-25), we have

$$\left(\frac{C}{T_0}+\frac{\lambda}{2}\right)(\theta_2^{+}-\theta_1^{+})=\frac{L}{T_0}+\left(\frac{C}{T_0}-\frac{\lambda}{2}\right)(\theta_2^{-}-\theta_1^{-})=\frac{L}{T_0};$$

this entails $\theta_2^{+}>\theta_1^{+}$, which forbids having $\theta_1^{+}\geq 0\geq\theta_2^{+}$. In this situation, conduction and heat storage have opposite effects and cancel each other.

Remark 5.4. The assumption $\lambda>2C/T_0$ is often not realistic because λ is proportional to the contact surface of the two pieces of ice and C is proportional to the volume of the pieces of ice. To have $\lambda>2C/T_0$, the contact surface has to be large compared to the volume — for instance, when the two pieces of ice are thin sheets. But in this case the contact surface with the atmosphere is also large in contradiction of the adiabatic assumption in the collision. Thus the assumption $\lambda>2C/T_0$ is not consistent with the adiabatic collisions, that is, collisions without heat exchange with the exterior.

6. Does rain give black ice when falling on frozen ground?

6.1. ***An application of the previous results.*** We may consider as a simplifying approximation that the ground behaves like a ball of frozen water. Thus we use the previous results and assume that λ is small with respect to C/T_0 and that there is no dissipation with respect to $[\beta_1]$ and $[\beta_2]$:

$$\Phi_1([\beta_1])=\Phi_2([\beta_2])=0.$$

A droplet of rain and the frozen ground before collision satisfy $\beta_1^{-}=1$, $\beta_2^{-}=0$, $\theta_1^{-}\geq 0$ and $\theta_2^{-}\leq 0$. We look for conditions such that the droplet of rain freezes, becomes black ice, and the ground remains frozen:

$$\beta_1^{+}=0,\qquad \beta_2^{+}=0. \tag{6-1}$$

Thus from (5-16), we have

$$\theta_1^{+}\leq 0,\qquad \theta_2^{+}\leq 0. \tag{6-2}$$

We assume that the collision is adiabatic and, for consistency, that λ is small with respect to C/T_0. Equations (5-6) and (5-7), with $C_1 = C_2 = C$, and using (6-1), give

$$C[\theta_1] = \tfrac{1}{2}\big(\mathcal{T} + 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big), \qquad C[\theta_2] = \tfrac{1}{2}\big(\mathcal{T} - \lambda T_0(\theta_2^- - \theta_1^-)\big).$$

By means of (5-20), conditions (6-2) are satisfied if and only if

$$(2C - \lambda T_0)\theta_1^- + \lambda T_0 \theta_2^- + \mathcal{T} + 2L \le 0, \qquad \lambda T_0 \theta_1^- + (2C - \lambda T_0)\theta_2^- + \mathcal{T} \le 0, \tag{6-3}$$

with $\theta_1^- \ge 0$ and $\theta_2^- \le 0$. Because of the hypothesis $2C - \lambda T_0 > 0$, it is always possible to satisfy conditions (6-3) by having θ_2^- negative enough, that is, by having the ground very cold. The maximum value of θ_2^- is given by $\theta_1^+ = 0$. It is

$$\theta_2^- = -\frac{\mathcal{T} + 2L}{\lambda T_0} - \frac{2C - \lambda T_0}{\lambda T_0}\theta_1^-, \quad \text{or} \quad \theta_2^- = -\frac{\mathcal{T} + 2L}{\lambda T_0} - \frac{2C}{\lambda T_0}\theta_1^-,$$

because λ is small with respect to C/T_0. As may be expected, the maximum value of θ_2^- is negative and decreasing when the dissipated work $\mathcal{T}$ is increasing and when θ_1^- is increasing [Caucci and Frémond 2007; Caucci 2006].

6.2. ***Another assumption: the ground is massive and its temperature remains constant.*** We assume the ground temperature remains constant in the collision. We get this property if the heat impulse capacity C_2 is very large compared to C_1. Thus we let $C_2 = \infty$ in formulas (5-6) and (5-7) and get the equations

$$C_1[\theta_1] = \frac{1}{2}\bigg(P^{\text{int}} D\Big(\frac{U^+ + U^-}{2}\Big) - 2L[\beta_1] + \lambda T_0\Big(\theta_2^- - \theta_1^- - \frac{[\theta_1]}{2}\Big)\bigg),$$

and $\theta_1^+ \in \partial I(\beta_1^+)$ — see (5-10) — assuming no dissipation with respect to $[\beta_1]$. They give

$$\Big(C_1 + \frac{\lambda T_0}{4}\Big)[\theta_1] + L[\beta_1] = \tfrac{1}{2}\big(\mathcal{T} + 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big),$$

and

$$\Big(C_1 + \frac{\lambda T_0}{4}\Big)\theta_1^+ + L\partial I^*(\theta_1^+) \ni \Big(C_1 + \frac{\lambda T_0}{4}\Big)\theta_1^- + \tfrac{1}{2}\big(\mathcal{T} + 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big),$$

where $I^*(\theta_1^+) = pp(\theta_1^+)$ is the dual function of I ($pp(x)$ is the nonnegative part of x). Assuming λ is small with respect to C/T_0, we have

$$C_1\theta_1^+ + L\partial I^*(\theta_1^+) \ni C_1\theta_1^- + \tfrac{1}{2}\big(\mathcal{T} + 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big),$$

with the following solutions:

(1) If

$$C_1\theta_1^- + \tfrac{1}{2}\big(\mathcal{T} + 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big) \le 0, \qquad \theta_1^+ \le 0, \qquad \theta_2^- \le \frac{(\lambda T_0 - 2C_1)}{\lambda T_0}\theta_1^- - \frac{(\mathcal{T} + 2L)}{\lambda T_0},$$

the droplet freezes. Its temperature is

$$\theta_1^+ = \theta_1^- + \frac{1}{2C_1}\big(\mathcal{T} + 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big).$$

(2) If $0 \le C_1\theta_1^- + \frac{1}{2}\big(\mathcal{T} + 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big) \le L$, the droplet freezes partially at $0°C$:

$$\theta_1^+ = 0.$$

(3) If $L \le C_1\theta_1^- + \frac{1}{2}\big(\mathcal{T} + 2L + \lambda T_0(\theta_2^- - \theta_1^-)\big)$, the droplet does not freeze. Its temperature becomes

$$\theta_1^+ = \theta_1^- + \frac{1}{2C_1}\big(\mathcal{T} + \lambda T_0(\theta_2^- - \theta_1^-)\big).$$

Note that the conditions for the droplet to freeze are similar under the two assumptions. The occurrence of black ice on roads due to rain falling on deeply frozen ground is predicted by this theory.

6.3. ***A more realistic assumption: the temperature of the ground is not uniform after collision.*** Under the two previous assumptions, the temperature of the ground is uniform after collision. It is clear that there is a local increase of the temperature where the droplet hits the ground but the temperature remains constant at some distance. Thus an interesting assumption is that the temperature of the ground is not uniform after collision: the temperature discontinuity $[\theta_2]$ becomes a function of x. This predictive theory is given in [Frémond 2001]. It is better but it has the disadvantage that closed form solutions are not available.

7. Conclusions

The thermomechanical theory of collisions involving phase change we have investigated is in agreement with everyday experiments.

We considered the collision of two pieces of ice. When they have different temperatures and collide, the dissipation due to the collision may be large enough to melt the warmest of them. We looked for conditions on the state quantities before the collision and on the dissipated work such that this phenomenon occurs. We showed that, if the dissipation is large, one piece of ice melts and the other remains frozen. For this to happen, the temperature of the coldest piece of ice has to be sufficiently cold.

We also studied the problem of warm rain falling on frozen ground, asking whether the rain freezes or the frozen ground thaws. We proved that the droplet of rain freezes if the ground is very cold. For this to occur, the temperature of the ground has to be lower than a maximum temperature, which decreases as the dissipated work and the temperature of the rain increase.

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ANNA MARIA CAUCCI: caucci@dm.unibo.it
Università di Bologna, Dipartimento di Matematica, Piazza di Porta S. Donato, 5, 40126 Bologna, Italy

MICHEL FRÉMOND: michel.fremond@lagrange.it
Università di Roma Tor Vergata, Laboratorio Lagrange, Dipartimento di Ingegneria Civile, Via del Politecnico, 1, 00133 Roma, Italy