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The physics and the chemistry of the heat pad

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Flexing a metallic disk triggers the crystallization of the supercooled sodium acetate solution contained in commercial heat pads. Many mechanisms have been proposed to explain the apparent nucleation of crystalline material. In this paper a simple experiment is described that demonstrates that nucleation is triggered by preserving seed crystals clamped between opposing metal surfaces. An explanation for the retention of the crystalline particles is the elevated melting point caused by very high local pressures. A series of thermophysical properties of the sodium acetate solution is also measured, including the available enthalpy upon crystallization of the supercooled substance, and liquid and solid phase specific heat capacities. © *2008 American Association of Physics Teachers.*
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I. INTRODUCTION

A heat pad can be purchased in almost every shape, size and color [see Fig. 1(a)]. The pad contains a supercooled liquid that at the flex of a disk, crystallizes and releases heat. Once used, put the heat pad in hot water until the crystals melt, let it cool, and it is ready to use again.

The substance inside the heat pad is sodium acetate, a salt hydrate that can be supercooled far below its freezing point without undergoing a phase transition from liquid to solid. The supercooled liquid is metastable because the spontaneous transition to the thermodynamically stable solid phase is hindered by a nucleation barrier that prevents the growth of macroscopic particles of crystalline material. Also contained in the heat pad is a trigger device that can be manipulated by the user to initiate the crystallization of the supercooled liquid [Figs. 1(b) and 1(c)]. When the material crystallizes, the energy associated with the phase transition, the latent heat of fusion, is released and the temperature increases to the melting/freezing point temperature of the substance, which for sodium acetate trihydrate is ≈58 °C.

Heat storing devices using supercooled salt hydrates (sodium acetate in particular) date back over 100 years.[1] The present form of the heat pad with the metallic trigger appeared in the late 1970s.[2] Their metallic strip activator inspired numerous patents from other inventors, and the trigger mechanism quickly evolved to the familiar metallic disk trigger of today's heat pads.

How do these triggers work? The explanation offered by many of the companies selling these products, that the flexing of the disk causes "a single molecule to crystallize,"[3] is not very convincing. By browsing through the extensive list of patents on the subject, we find that there are almost as many mechanisms as there are inventors. Proposed effects include nucleation by friction,[4–6] tearing at the ends of slits exposing a fresh metal surface,[2,7] local compression of the solution confined in the slit,[8] small particles broken off from slit surfaces acting as heterogeneous nucleation centers,[9] and oscillation waves created by friction as the disk is snapped.[10]

In Sec. II we demonstrate with a simple bench top experiment that none of these mechanisms is correct. Instead, the triggers work by preserving crystal fragments isolated from the melt. These particles act as seeds that are introduced in the supercooled liquid when the trigger is flexed. The explanation for why seeds are preserved at temperatures above the normal melting point (during melting of the heat pad contents) is that the microscopic particles are trapped between opposite metal surfaces and the high local pressure causes an elevated melting point.[11]

In Sec. III the relevant thermophysical properties, including the latent heat and specific heat capacity of the sodium acetate material contained in the heat pads, are measured using a simple method requiring only a test tube and a temperature logger.

II. TRIGGERING CRYSTALLIZATION

The most common trigger device is a thin concave metal disk as shown in Fig. 1(b). Flex or snap the disk by pressing it in the center with your fingers, and observe crystals growing radially outward from a series of slits in the thin metal disk. In the production process these slits are made by stamping a sharp dye on the disk, cutting or tearing the metal apart. The "flaps" are then flattened so that the opposing torn edges of the slits are pressed against each other. A different type of trigger that has been introduced more recently is a simple metal spring with tightly wound coils as shown in Fig. 1(c). The growing crystals appear from between the coils when the spring is bent in the supercooled solution.

Although there have been great improvements in trigger reliability and user friendliness, the modern trigger devices are not without problems. Common complaints are "trigger-happy" devices that go off unintentionally, and triggers that stop working after a while. We shall soon see why.

An experiment was set up to test the crystallization triggering ability of a selection of triggers. Ten mini "heat pads" were prepared by filling small sealable plastic bags with 10 ml sodium acetate melt; one trigger was added to each bag. Disks 1–4 were typical stainless steel heat pad flexible disks with cut slits. Springs 5–8 were tight single coil stainless steel springs also found in heat pads. Springs 9 and 10 were standard lab springs.

The bags were placed in a heat bath and maintained at 90 °C until all the material had melted. The bags were subsequently cooled to 15 °C (highly supercooled) before the triggers were flexed, and the success/failure of the triggering was recorded for each flex. The experiments differed in only one respect; two different treatments of the triggers were tested: Activation: The triggers were flexed in the crystallized sodium acetate trihydrate at 15 °C prior to melting in order to introduce crystal particles between the metal surfaces of the triggers (the slits of the disks, the coils of the

Fig. 1. (Color online) (a) The "hot gel" and "warm mate" heat pads and a selection of triggers. Close up images of (b) the flexible disc and (c) the spring type trigger. The disk trigger is 19 mm in diameter.

springs). Deactivation: The triggers were flexed repeatedly in the melted solution at 90 °C in order to expose and melt crystal particles harboring between the metal surfaces, so that the triggers would be free of any crystalline material at the time of supercooling.

In Fig. 2 successful crystallizations are represented by individual bars for each trigger plotted against 25 experimental runs alternating between activated and deactivated triggers. The first six trials were conducted with activated triggers, and Fig. 2 shows that all ten triggers crystallized the supercooled solution. The triggers were deactivated for the following six trials, and as a result most of the triggers lost their ability to crystallize the solution as indicated. Upon reactivation of the triggers by the procedure we have described, they regained their ability to produce crystallization. The difference in success between the two experimental conditions is clear. When flexing the triggers in the crystal, almost all the triggers initiated crystallization, usually at the first flex. After the triggers are flexed in the melt (deactivation), all but one or two lost their ability to crystallize the supercooled solution. (Disk 3 kept crystallizing the solution even after repeated deactivation, but the failure to deactivate this trigger might be due to the difficulty of making sure that all the slit surfaces had been properly exposed to the melt. The deactivation procedure is more well defined for the springs, where the surfaces can be kept parted for some time.)

These observations indicate that the triggers work by preserving crystalline seed particles at a high temperature while the surrounding material melts. The seed particles must be isolated within the trigger to allow the solution to become supercooled. When the trigger is manipulated, these seeds are introduced in the supercooled solution where they act as heterogeneous nucleation centers initiating the crystallization. Hence, the triggers must be activated by exposure to crystalline material to become effective, and can be deactivated by the removal of these seeds.

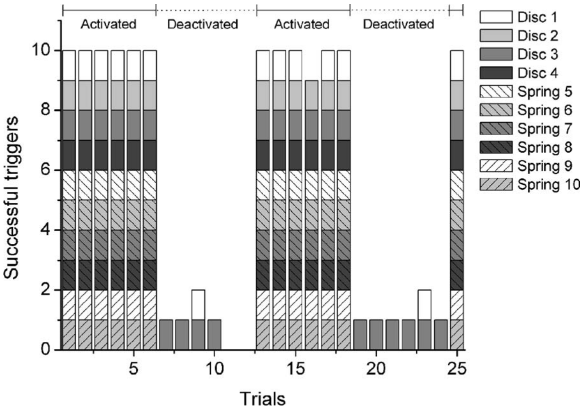

Fig. 2. Stacked bar chart where the bars represent successful crystallization for the respective triggers. Activation or deactivation treatments are indicated above the chart.

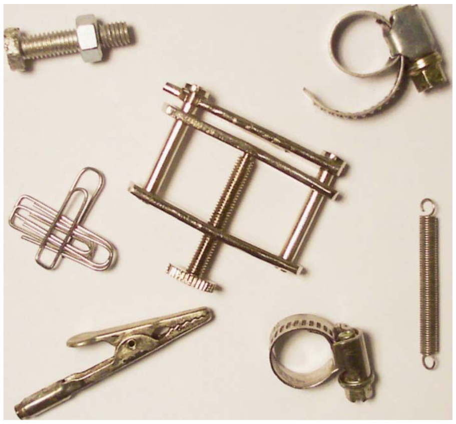

Fig. 3. (Color online) The next generation triggers?

Other physical mechanisms that have been proposed to explain the induced crystallization, such as friction and exposure of fresh metal surface, can be rejected on the grounds that they would all be unaffected by the imposed experimental conditions. The observations made by frustrated heat pad users may be explained by the fact that the heat pad will be triggered unintentionally if a small external disturbance causes the release of at least one of the seeds. Alternatively, if no seed particles are retained after repeated use, the trigger will stop working.

The heat pad triggers are characterized as having opposing surfaces in one form or another. With this property in mind, a selection of lab appliances were put to the "trigger test" (see Fig. 3). The various tube clamps, screw and nut, bunch of paper clips, lab spring, and crocodile clip all worked well as crystallization triggers after the activation procedure. The solution supercooled without fail, and crystallization was triggered by loosening the clamps, twisting the nut, etc.

Barrett and Benson found that sodium acetate trihydrate crystals, when clamped between two pieces of various materials, can be heated above the normal melting point and still nucleate the supercooled solution.[11] The maximum survival temperature of the clamped crystal was found to increase with increasing hardness of the material it was clamped between. The results were discussed in Refs. 12 and 13, and it was concluded that the maximum measured survival temperature was the pressure dependent melting point of the crystal particles trapped in regions of extremely high pressure at the contact junctions between the two clamping substrates. An alternative explanation, that surface interactions are responsible for the elevated melting point, was suggested by Rogerson and Cardoso.[14,15]

When two rough surfaces are pressed together, the protruding asperities that first make contact undergo plastic deformation until the area of real contact, ΔA, becomes large enough that the contact pressure integrated over ΔA balances the force that presses the surfaces together.[16] This effective contact area is surprisingly small compared to the apparent contact area and can be estimated by dividing the compressing force, F, by the penetration hardness, σ_c, of the material:

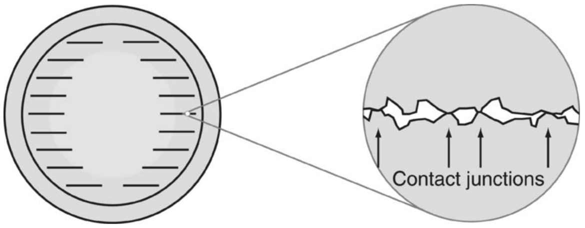

Fig. 4. A microscopic view of the opposing slit surfaces of the disk trigger. The local pressure at the contact junctions depends on the plastic yield hardness of the substrate.

$\Delta A = F/\sigma_c$. The penetration hardness for different steel materials is in the range of $1-7\times 10^9$ N/m^2, which is equivalent to contact pressures of approximately 10 000–70 000 atm. The diameter of one contact junction is typically ≈ 10 μm, and increased load results in new areas of contact being formed such that the area of real contact is proportional to the load. Most engineered surfaces, except when polished, are expected to have essentially all junctions in a state of incipient plastic flow.[16]

Crystalline material trapped in cracks or suitable locations at the contact junctions between two surfaces would thus experience extremely high pressures (see Fig. 4). The change in melting point of the crystalline material, ΔT, corresponding to a change in pressure, ΔP, is given by the Clapeyron equation

$$\frac{\Delta T}{\Delta P} = \frac{T_e(V_l - V_s)}{L}, \tag{1}$$

where T_e is the melting temperature at the reference pressure, V_l and V_s are the specific volume of the liquid and solid phase, respectively, and L is the latent heat of fusion. (Note that $\Delta V = V_l - V_s$ and L generally are pressure dependent). The melting point thus increases with increased pressure for substances that expand on melting (as most substances do), and the trapped seed crystals at the plastic yield pressure of the substrate would therefore have a significantly raised melting temperature.

Barrett and Benson[11] found the maximum survival temperature of sodium acetate trihydrate clamped between stainless steel substrates to be about 166 °C. For the case of the heat pad, the situation is as follows: The solidified heat pad content is melted by immersing the bag in hot water. Trapped seed crystals in the trigger device remain in the solid phase because the temperature does not reach their elevated high pressure melting point. The heat pad is able to supercool when the sodium acetate trihydrate is completely melted, except for the trapped seeds isolated within the trigger. This isolation is broken when the trigger surfaces are parted (flexed), whereby the particles become exposed to the supercooled liquid and act as seeds for further crystal growth.

III. LATENT HEAT

Most heat pads contain sodium acetate trihydrate due to its convenient melting point, the large amount of latent heat it releases during crystallization, and its ability to remain in a supercooled state for months and even years. Sodium acetate trihydrate is, as its name implies, a salt hydrate. In liquid form the Na^+ and CH_3COO^- ions are soluble in water, and when it crystallizes, three moles of water for each mole of salt are incorporated into the crystalline structure:

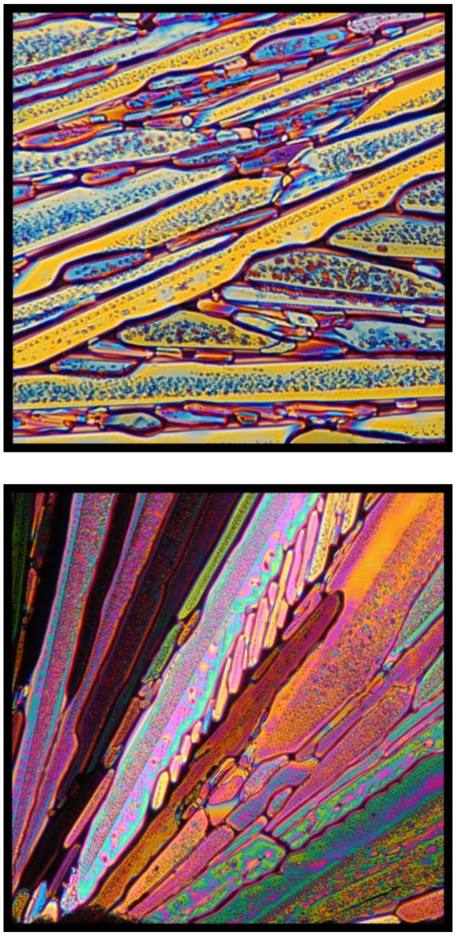

Fig. 5. (Color online) The art of sodium acetate trihydrate crystals. A drop of the melt was placed between two microscope slides, and crystallization of the supercooled liquid was seeded from one edge. The images show the polycrystalline structure observed between crossed polarizers in a microscope using a 5× objective.

$$Na^+(aq) + CH_3COO^-(aq) \rightarrow NaCH_3COO \cdot 3H_2O(s). \tag{2}$$

The crystals grow quickly, approximately 5 mm/s,[17] and the solid phase has a polycrystalline structure resulting from the dendritic growth process (Fig. 5).

We now describe a simple method that can be used to determine a range of thermophysical properties of sodium acetate trihydrate using only a temperature logger and some simple calculations. To perform controlled experiments we replace the heat pad container with a glass test tube.

Sodium acetate trihydrate was added to a test tube and heated up to 70 °C in a water bath. When all the material had melted, the test tube was placed on a table with an immersed temperature sensor. Figure 6 shows the temperature as the content of the test tube cooled by heat loss to the surroundings. Equilibrium was reached, and after 6 h the supercooled sodium acetate solution was seeded, whereby the sodium acetate immediately crystallized to the trihydrate. The graph shows the sudden temperature increase as the stored latent heat is released, and the temperature stabilizes at the solid/liquid phase transition temperature, which we determine to be 56.8 °C. The system is maintained at this temperature until most of the substance is crystallized (how

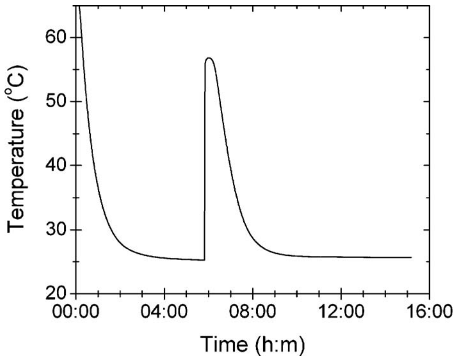

Fig. 6. Temperature as a function of time as the sodium acetate becomes supercooled, crystallizes, and cools again.

long depends on the rate of heat loss from the container). When the phase transition is more or less complete, the temperature again falls to that of the surroundings.

A reference experiment with purified water replacing sodium acetate in the test tube allows us to determine the heat transfer coefficients for the system. Assuming that the heat loss is limited by the tube surface to air heat transfer, the sodium acetate filled test tube experiences the same rate of heat loss, which depends only on the temperature difference between the system and the ambient. From the measured temperature curve we can construct the enthalpy-temperature diagram of the material, the amount of stored energy as a function of temperature, by adding up the total heat transferred to the surroundings over the temperature range studied (see Appendix).[18]

Figure 7 shows the enthalpy-temperature diagram based on the temperature readings presented in Fig. 6. The sequence of events is as follows: As the sodium acetate cools by heat loss to the surroundings, the enthalpy decreases linearly with temperature due to the specific heat capacity of the liquid (line segment 1 in Fig. 7). In the supercooled state the enthalpy and temperature remain constant. Upon seeding the temperature increases at constant enthalpy to the phase transition temperature (line 2). During the phase transition (line 3) the temperature is maintained more or less constant while the enthalpy decreases steadily due to further heat losses to the surroundings. Toward the end of the solidification process the temperature again starts to decrease, and finally the decrease in the stored enthalpy is due to the solid state heat capacity of the substance (line 4).

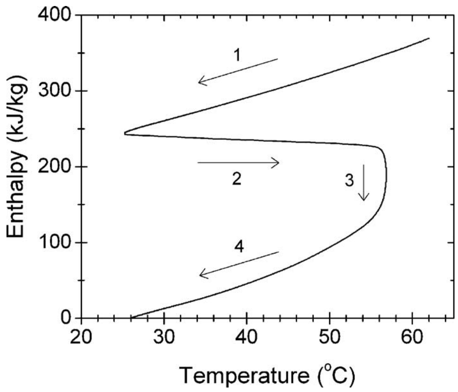

Fig. 7. Enthalpy-temperature diagram for supercooling sodium acetate reconstructed from the temperature plot in Fig. 6. The arrows indicate time in the experiment: (1) initial cooling of liquid phase, (2) crystallization, (3) release of latent heat, and (4) finally cooling of the solid phase to room temperature.

The enthalpy-temperature diagram gives a visualization of some of the important thermophysical properties of the sodium acetate material. The liquid and solid phase specific heat capacities for instance, are given by the slope of the enthalpy curve, $c_p = dH/dT$, in the respective phases.

The amount of heat available to the heat pad user upon crystallization was determined from the graph to be 137 kJ/kg (counting only heat released during the phase transition and while the temperature is above 50 °C). Although this amount is sufficient to keep your hands warm for a while, we see from line 1 in Fig. 7 that a large amount of heat is lost to the surroundings during the initial supercooling stage. This amount will depend on the temperature at which the supercooled substance is kept. The total latent heat in the phase transition is 254.6 kJ/kg (measured between 50 °C and the phase transition temperature prior to supercooling.) Thus, only about 54% of the energy stored as latent heat is available to the heat pad user after supercooling. The rest of the energy is lost to the surroundings during the initial cooling and is equivalent to the amount of released latent heat spent on increasing the temperature to the phase transition temperature as the crystallization is initiated.

IV. CONCLUSION

The metastable nature of supercooled sodium acetate, and the rapid crystal growth upon seeding with subsequent release of latent heat, has made it a popular choice for science demonstrations of phase transitions and exothermic reactions.[19]

Despite a long history and many patents, there seems to be widespread confusion regarding the physical mechanism for how the trigger devices contained in these heat pads work. We have described a simple demonstration that indicates that the triggers work by preserving microscopic seed crystals clamped between the opposing metal surfaces of these triggers. The crystalline particles remain within the device and isolated from the supercooled liquid until the trigger is manipulated by the user, at which time the exposed particles act as seeds for the crystal growth.

We have also described a procedure for determining the relevant thermophysical properties of the sodium acetate material contained in the heat pad using a simple experimental setup. The enthalpy-temperature diagram gives properties such as the latent heat of the material, the amount of heat available upon crystallization, and the liquid and solid phase specific heat capacities.

The experiments are easy to perform, require only basic equipment, and provide important insights into as supercooling, seeding, crystal growth, latent heat, heat capacity, and phase transitions. The experiments and the associated analysis are therefore well suited for demonstrations and practical exercises in undergraduate labs.

Finally, a piece of advice: Regardless of the type of trigger used, manufacturers of heat pads should add a sentence to the user instructions that is guaranteed to increase customer satisfaction: “Flex once or twice before melting to ensure that the trigger is fully charged with crystal seeds.”

ACKNOWLEDGMENT

Many thanks to John Rekstad for useful discussions.

APPENDIX: FROM TEMPERATURE CURVE TO ENTHALPY DIAGRAM

A reference experiment with a known mass m of water in the test tube allows us to determine the temperature-dependent heat transfer from the test tube. The temperature is recorded at regular time intervals as the system cools from an elevated initial temperature by heat loss to the surroundings. The heat loss from the reference tube during the time interval Δt is given by

$$q(t) = (m_w c_{p,w} + m_t c_{p,t} + m_s c_{p,s}) \frac{\Delta T(t)}{\Delta t}, \tag{A1}$$

where c_p is the specific heat capacity at constant pressure. The subscripts w, t, and s refer to water, test tube, and temperature sensor, respectively. The resultant heat loss values are plotted against the temperature difference between the system and the surrounding air, and a second degree polynomial fit to the data yields the first and second order heat transfer coefficients k_1 and k_2 in Eq. (A2).

Having determined the temperature-dependent heat transfer in the reference experiment, we can calculate the time-dependent heat release from the system containing sodium acetate as a function of the temperature difference between the system and the ambient temperature T_a:

$$q(t) = k_1(T(t) - T_a(t)) + k_2(T(t) - T_a(t))^2. \tag{A2}$$

The heat loss from the sodium acetate material, q_{SA}, is found by subtracting from q the specific heat contribution from the test tube and the sensor. The enthalpy change in each time interval is given by

$$\Delta H(T) = \frac{q_{SA}\Delta t}{m_{SA}}. \tag{A3}$$

The enthalpy-temperature diagram is generated by plotting the cumulative enthalpy change as a function of temperature, choosing an arbitrary reference point. For a more detailed account of the experimental procedure, see Ref. 18 and references therein.

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