Entropy is Supercool

Up to this point, the discussion of entropy woven throughout the last many columns have featured entropy as a phenomenological parameter derived from the various equivalent formulations of the second law and clever, inventive ways of decomposing cyclical processes using the reversible steps of the Carnot cycle. In this post, it is worth taking a breather from all the abstract theory by looking at a particularly instructive problem that has been used in a variety of pedagogical contexts: the situation of supercooled water. This problem illustrates the thinking that a classical thermodynamicist (i.e. someone who is not using the molecular interpretation) would use. The precise wording that we’ll follow is taken from problem 20.21 of the *Fundamentals of Physics, 10th Edition – Halliday & Resnick, Walker*, which reads:

\*\*Energy can be removed from water as heat at and even below the normal freezing point ($0.0^{\circ} C$ at atmospheric pressure) without causing the water to freeze; the water is then said to be supercooled. Suppose a $1.00 g$ water drop is supercooled until its temperature is that of the surrounding air, which is at $-5.0^{\circ} C$. The drop then suddenly and irreversibly freezes, transferring energy to the air as heat. What is the entropy change for the drop?\*\*

This problem is interesting because the sudden and irreversible (to be verified later) transition of the water from a liquid drop to solid shard is not representable as a well-defined sequence of equilibrium states. Nonetheless, we can calculate the change in entropy by imagining a reversible process that connects the initial state (supercooled drop) to the final state (frozen shard) as being made up of three legs. By analyzing the changes along each reversible leg, we can arrive at the total change of the entropy and then, by relying on the fact that everything is now expressed in terms of state variables, we can let go of any appeal to reversibility. Effectively, this three-legged process is a scaffold that can be thrown away once the underlying structure has been erected and the change in entropy obtained.

In the first leg we reversibly heat the drop from its supercooled temperature ($T\_C = 268 K$) until it is at its freezing point ($T\_H = 273 K$). On the second leg, we allow the drop to freeze naturally and reversibly into a shard of ice. In the third leg, we finally cool the shard of ice back down to the $T\_C$.

For the first and third legs, we can relate the change in temperature $dT$ to the quantity of heat $dQ$ exchanged between the water (the system) and the surrounding air (the environment) as

\[dQ = m c dT \; ,\]

where $c$ is the specific heat capacity, which is assumed, for simplicity, to be constant over the temperature range, depending only on the phase of the material, and $m$ is the mass of the water. For water, the specific heat in liquid form is cited by the text as $c\_L = 4.19 J/gK$ and the specific heat in solid form is $c\_S = 2.22 J/gK$.

For the second leg, we use the standard definition of the latent heat of fusion, $L\_F$ to tell us that the heat shed to the environment is

\[ dQ\_{freeze} = -L\_F m \; ; \]

for water $L\_F = 333 J/g$. Note that the sign is negative since heat moves out of the drop to the environment.

The changes in entropy along legs one and three are:

\[ \Delta S\_{leg\_1} = \int\_{T\_C}^{T\_H} \frac{dQ}{T} = \int\_{T\_C}^{T\_H} \frac{m c\_L dT}{T} = m c\_L \ln \left( \frac{T\_H}{T\_C} \right) \; \]

and

\[ \Delta S\_{leg\_3} = \int\_{T\_C}^{T\_H} \frac{dQ}{T} = \int\_{T\_C}^{T\_H} \frac{m c\_S dT}{T} = - m c\_S \ln \left( \frac{T\_H}{T\_C} \right) \; . \]

The change in entropy along leg two (reversible freezing at $T\_H$) is

\[ \Delta S\_{leg\_2} = \frac{dQ}{T\_H} = \frac{L\_F m}{T\_H} \; . \]

Combining leads to a total change in entropy of the drop

\[ \Delta S\_{drop} = m ( c\_L – c\_S ) \ln \left( \frac{T\_H}{T\_L} \right) - \frac{L\_F m}{T\_H} \; .\]

Since the drop freezes suddenly and irreversibly, one might think that the $\Delta S$ should be positive but this conclusion ignores the fact that the second law only says that the total, universal entropy change should be positive for an irreversible process. The numerical computation is

\[ \Delta S = 1g (4.19-2.22) J/gK \ln(273/268) + \frac{333 J/g \cdot 1 g}{273 K} = -1.18 J/K \; .\]

Our faith in thermodynamics will be bolstered if we can show that the total entropy has increased. The change in the entropy of the surroundings is given by

\[ \Delta S\_{sur} = \frac{dQ\_2}{T\_L} = \frac{ L\_F m}{T\_L} \; . \]

Note that this expression is almost identical to that used in leg 2 of the reversible process with the single change that the heat is delivered to the environment at the lower temperature $T\_L$ instead of the higher one.

The total change in the entropy of the universe is

\[ \Delta S\_{uni} = \Delta S\_{drop} + \Delta S\_{sur} = m ( c\_L – c\_S ) \ln \left( \frac{T\_H}{T\_L} \right) + L\_F m \left( \frac{1}{T\_L} - \frac{1}{T\_H} \right) \; .\]

Putting numbers to it gives

\[ \Delta S\_{uni} = -1.18 J/K + \frac{333 J/g \cdot 1 g}{268 K} = -1.18 J/K + 1.24 J/K = 0.059 J/K > 0 \; .\]

The fact that the overall universal entropy increases rigorously what we already expected from the framing of the problem – that the sudden freezing of the supercooled drop is an irreversible process.

Finally, it is worth noting two points that follow from the observation that $c\_L > c\_S$ for water and $T\_L < T\_H$, by definition for supercooling. First, the naïve model developed here suggests that water can be supercooled to any temperature since $\Delta S\_{uni}$ is always positive. Clearly water is more subtle in its behavior as evidenced by the fact that there is an [observed lower limit of $-48C$](https://www.sciencedaily.com/releases/2011/11/111123133123.htm) below which supercooled water cannot exist. Second, isn’t at all clear that the heat capacity of an arbitrary material in a liquid phase should always be greater than that in its solid phase, although basic considerations of statistical mechanics suggests that it should be.