The Zeroth Law of Thermodynamics **Felix Flicker**

We can deduce at least two facts about the zeroth law of thermodynamics from its name: first, that it must be necessary to establish before the other laws can be used (otherwise it would have been named the fourth law); second, that the necessity of stating this fact was realised after the other laws were already assigned their names. Together, these observations warn us that the zeroth law is of a vital importance, but that it features a subtlety which makes it easy to overlook.

The zeroth law establishes properties of *thermal equilibrium*, which are key to setting up the wider study of thermodynamical systems.

> **Thermal Equilibrium:**
> Two systems are said to be in thermal equilibrium if there is no net flow of energy between them when they are allowed to exchange heat.

A thermodynamical 'system' is simply a collection of matter or region of space – it could be separated from its surroundings by a barrier, but it need not be.

> **Lieb and Yngvason's statement of the Zeroth Law of Thermodynamics[1]:**
> *Thermal equilibrium is an equivalence relation between pairs of thermodynamical systems.*

The idea of an 'equivalence relation' comes from mathematical logic. Denoting equivalence by the symbol $\equiv$, the following three conditions hold:

$$\begin{aligned} &(i) \quad A \equiv A \quad (\textit{reflexivity}) \\ &(ii) \quad A \equiv B \text{ implies } B \equiv A \quad (\textit{symmetry}) \\ &(iii) \quad \text{if } A \equiv B \text{ and } B \equiv C \text{ then } C \equiv A \quad (\textit{transitivity}). \end{aligned}$$

At first it might seem difficult to think of any relations which do not obey them, but a little thought reveals many cases. Condition (i), reflexivity, is obeyed by the relation 'is equal to': $A = A$. But it is not obeyed by the relation 'is greater than': $A \not> A$. On the other hand, the relations 'is equal to' and 'is greater than' are both transitive. An intuitive example of a non-transitive relation is 'beats' in *Stone Paper Scissors*: stone beats scissors, and scissors beat paper, but paper beats stone. Another is non-transitive dice (Fig 1). Consider the set of dice with sides

$$\begin{aligned} &A : \{2, 2, 4, 4, 9, 9\} \\ &B : \{1, 1, 6, 6, 8, 8\} \\ &C : \{3, 3, 5, 5, 7, 7\}\,. \end{aligned}$$

The numbers on each die add to 30. To work out the probability of one die beating another, we can just consider all $6 \times 6 = 36$ possible outcomes of the combined two-dice roll. Actually, since each die has two copies of each number, we only need to consider $3 \times 3 = 9$ options. The entry in the table indicates the winner:

	$A:2$	$A:4$	$A:9$
$B:1$	A	A	A
$B:6$	B	B	A
$B:8$	B	B	A

	$B:1$	$B:6$	$B:8$
$C:3$	C	B	B
$C:5$	C	B	B
$C:7$	C	C	B

	$C:3$	$C:5$	$C:7$
$A:2$	C	C	C
$A:4$	A	C	C
$A:9$	A	A	A

By counting the entries we see that the probability that A beats B is 5/9: $P(A > B) = \frac{5}{9}$. Similarly, $P(B > C) = \frac{5}{9}$. So then it would be quite reasonable to think that, since A beats B on average, and B beats C on average, that A beats C on average. But in fact C beats A with exactly the same probability,

[1] E. H. Lieb and J. Yngvason, *The physics and mathematics of the second law of thermodynamics*, Physics Reports 310, 1–96 (1999)

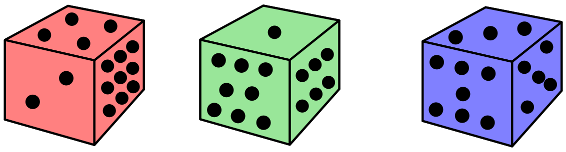

Figure 1: Non-transitive dice, where each die has two copies of each number. The numbers on each die add to 30. Left beats middle with probability 5/9, middle beats right with probability 5/9, and right beats left with probability 5/9. The relation 'beats on average' is not transitive.

5/9! Non-transitive dice demonstrate an important point: 'x beats y on average' is not transitive. The statement of the zeroth law, that thermal equilibrium is transitive, is therefore of great importance when it comes to attempting to derive the laws of thermodynamics from the microscopic behaviour of particles in *statistical mechanics*, which relies heavily on probability theory.

Consider a set of thermodynamical systems, which need not be in thermal equilibrium with one another. The zeroth law tells us that thermal equilibrium is an equivalence relation between pairs of thermodynamical systems. This means that we can sort the systems into *equivalence classes*, such that each equivalence class contains only systems which are in thermal equilibrium (or would be, if allowed to exchange heat). Any systems which are not in thermal equilibrium must be in different equivalence classes. In this way, we can label each system according to which equivalence class it is in, and each system will receive precisely one label. As far as the zeroth law is concerned, these labels can be arbitrary, provided they are different between different equivalence classes. A very convenient choice of label is to assign each class a real number which we call the *temperature*(!).

The zeroth law is often summarized as 'thermometers work'. When we say that a system has a given temperature, we are saying that a thermometer would be in thermal equilibrium with the system when the thermometer had a certain reading on a certain temperature scale (say, some height of mercury along a partially-evacuated tube). If you find that a thermometer with a given height of mercury is in thermal equilibrium with your mouth, and that the thermometer with the same height of mercury is also in thermal equilibrium with a bath of water, the zeroth law tells you that you will be in thermal equilibrium with the water. On the other hand, if either you or the water is *not* in thermal equilibrium with the thermometer, you can be certain you will not be in thermal equilibrium with the water, and heat transfer would take place were you to get in the bath.

The zeroth law does not make any direct reference to temperature. Nevertheless, by establishing thermal equilibrium as an equivalence relation – obeying reflexivity, symmetry, and transitivity – it remains vital in identifying the validity of thermometers. To see this, consider trying to make the equivalent of a thermometer for a non-transitive system. For example, say you are a zoo keeper, and the different animal enclosures are to be thought of as the analogues to different thermodynamical systems. Cost-cutting measures have forced you to move one species of animal in with another. You'd better make sure that when the species are brought into contact, the behaviour of both species remains unchanged (the analogue of thermal equilibrium). As a form of thermometer, you try using a small test-animal, say a tortoise, which you introduce into each enclosure. You place the tortoise in with the zebras, and nothing much happens. They are in equilibrium. Then you place the tortoise in with the lions, and nothing much happens. They too are in equilibrium. So you deduce that when you place the lions in with the zebras, nothing much will happen, and they too will be in equilibrium. Unfortunately, 'x eats y' is *not* a transitive relation. Without the zeroth law, things go rather badly.

Key Points

- Two systems are said to be in *thermal equilibrium* if there is no net flow of energy between them when they are allowed to exchange heat.
- The zeroth law: *Thermal equilibrium is an equivalence relation between pairs of thermodynamical systems.*
- Thermodynamical systems can be assigned a label (indicating their *equivalence class*) such that if their label agrees with that of another system, the two will be in thermal equilibrium if allowed to exchange heat. If the labels differ, they are guaranteed *not* to be in thermal equilibrium initially, and heat transfer must occur.
- The equivalence class label may be chosen to be a real number, temperature, although this is not dictated by the zeroth law.
- The zeroth law establishes the foundation necessary for thermometry.