

# Use of Thermodynamics and Statistical Mechanics in Describing the Real World\*

Yaneer Bar-Yam

*New England Complex Systems Institute, Cambridge, MA 02139*

(Dated: February 26, 2019)

How do we generalize the notions of thermodynamics that we have just described to apply to more realistic situations? The assumptions of thermodynamics—that systems are in equilibrium and that dividing them into parts leads to unchanged local properties—do not generally apply. The breakdown of the assumptions of thermodynamics occurs for even simple materials, but are more radically violated when we consider biological organisms like trees or people. We still are able to measure their temperature. How do we extend thermodynamics to apply to these systems?

We can start by considering a system quite close to the thermodynamic ideal—a pure piece of material that is not in equilibrium. For example, a glass of water in a room. We generally have no trouble placing a thermometer in the glass and measuring the temperature of the water. We know it is not in equilibrium, because if we wait it will evaporate to become a vapor spread out throughout the room (even if we simplify by considering the room closed). Moreover, if we wait longer (a few hundred years to a few tens of thousands of years), the glass itself will flow and cover the table or flow down to the floor, and at least part of it will also sublime to a vapor. The table will undergo its own processes of deterioration. These effects will occur even in an idealized closed room without considerations of various external influences or traffic through the room. There is one essential concept that allows us to continue to apply thermodynamic principles to these materials, and measure the temperature of the water, glass or table, and generally to discover that they are at the same (or close to the same) temperature. The concept is the separation of time scales. This concept is as basic as the other principles of thermodynamics. It plays an essential role in discussions of the dynamics of physical systems and in particular of the dynamics of complex systems. The separation of time scales assumes that our observations of systems have a limited time resolution and are performed over a limited time. The processes that occur in a material are then separated into fast processes that are much faster than the time resolution of our observation, slow processes that occur on longer time scales than the duration of observation, and dynamic processes that occur on the time scale of our observation. Macroscopic averages are assumed to be averages over the fast processes. Thermodynamics allows us to deal with the slow and the fast processes but only in very limited ways with the dynamic processes. The dynamic processes are dealt with separately by Newtonian mechanics.

Slow processes establish the framework in which thermodynamics can be applied. In formal terms, the ensemble that we use in thermodynamics assumes that all the parameters of the system described by slow processes are fixed. To describe a system using statistical mechanics, we consider all of the slowly varying parameters of the system to be fixed and assume that equilibrium applies to all of the fast processes. Specifically, we assume that all possible arrangements of the fast coordinates exist in the ensemble with a probability given by the Boltzmann probability. Generally, though not always, it is the microscopic processes that are fast. To justify this we can consider that an atom in a solid vibrates at a rate of  $10^{10}$ - $10^{12}$  times per second, a gas molecule at room temperature travels five hundred meters per second. These are, however, only a couple of select examples.

Sometimes we may still choose to perform our analysis by averaging over many possible values of the slow coordinates. When we do this we have two kinds of ensembles—the ensemble of the fast coordinates and the ensemble of the different values of the slow coordinates. These ensembles are called the annealed and quenched ensembles. For example, say we have a glass of water in which

there is an ice cube. There are fast processes that correspond to the motion of the water molecules and the vibrations of the ice molecules, and there are also slow processes corresponding to the movement of the ice in the water. Let's say we want to determine the average amount of ice. If we perform several measurements that determine the coordinates and size of the ice, we may want to average the size we find over all the measurements even though they are measurements corresponding to different locations of the ice. In contrast, if we wanted to measure the motion of the ice, averaging the measurements of location would be absurd.

Closely related to the discussion of fast coordinates is the ergodic theorem. The ergodic theorem states that a measurement performed on a system by averaging a property over a long time is the same as taking the average over the ensemble of the fast coordinates. This theorem is used to relate experimental measurements that are assumed to occur over long times to theoretically obtained averages over ensembles. The ergodic theorem is not a theorem in the sense that it has been proven in general, but rather a statement of a property that applies to some macroscopic systems and is known not to apply to others. The objective is to identify when it applies. When it does not apply, the solution is to identify which quantities may be averaged and which may not, often by separating fast and slow coordinates or equivalently by identifying quantities conserved by the fast dynamics of the system.

Experimental measurements also generally average properties over large regions of space compared to microscopic lengths. It is this spatial averaging rather than time averaging that often enables the ensemble average to stand for experimental measurements when the microscopic processes are not fast compared to the measurement time. For example, materials are often formed of microscopic grains and have many dislocations. The grain boundaries and dislocations do move, but they often change very slowly over time. When experiments are sensitive to their properties, they often average over the effects of many grains and dislocations because they do not have sufficient resolution to see a single grain boundary or dislocation.

In order to determine what is the relevant ensemble for a particular experiment, both the effect of time and space averaging must be considered. Technically, this requires an understanding of the correlation in space and time of the properties of an individual system. More conceptually, measurements that are made for particular quantities are in effect made over many independent systems both in space and in time, and therefore correspond to an ensemble average. The existence of correlation is the opposite of independence. The key question (like in the case of the ideal gas) becomes what is the interval of space and time that corresponds to an independent system. These quantities are known as the correlation length and the correlation time. If we are able to describe theoretically the ensemble over a correlation length and correlation time, then by appropriate averaging we can describe the measurement.

In summary, the program of use of thermodynamics in the real world is to use the separation of the different time scales to apply equilibrium concepts to the fast degrees of freedom and discuss their influence on the dynamic degrees of freedom while keeping fixed the slow degrees of freedom. The use of ensembles simplifies consideration of these systems by systematizing the use of equilibrium concepts to the fast degrees of freedom.

\* Adapted from [Dynamics of Complex Systems Section 1.3.5](#).