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Questions and Answers

Irreversibility and the Thermodynamic Limit

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It is shown that the thermodynamic limit may be highly misleading when used in an attempt to resolve the paradoxes associated with the problem of irreversibility.

KEY WORDS: Irreversibility; thermodynamic limit; statistical mechanics.

The problem of "irreversibility" arose due to apparent contradictions between properties of the microscopic laws of physics and the observed behavior of macroscopic systems. These paradoxes were originally pointed out by Loschmidt(1) ("Umkehreinwand" using time reversal invariance) and Zermelo(2) ("Wiederkehreinwand" using Poincaré's(3) theorem).

It has long been popular to circumvent Zermelo's paradox by beginning discussions of irreversibility with the "thermodynamic limit." This step has been traditionally justified by two arguments:

1. The average "period" of a Poincaré cycle for a normal macroscopic system is far longer than the duration of any earth-bound experiment, so that taking it to be infinite is a good approximation.

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2. Several macroscopic observables of interest have equilibrium fluctuations that are proportional to $N^{-1/2}$. Since these fluctuations are usually very small, taking them to be zero is also a good approximation.

These arguments are, of course, good as far as they go. However, there are other considerations which they do not take into account.

Since irreversibility and the approach to equilibrium are time-dependent phenomena, the time scale is of major importance. In particular, we would like to call attention to the time required for particles or information to return from the walls of a normal macroscopic system. This "echo" or "reflection" time t_R is given by

$$t_R = L/v \tag{1}$$

where L is a typical dimension of the system and v is some characteristic velocity (sound velocity, average speed of particles, speed of light, etc.). For most earth-bound experiments t_R is either of the same order of magnitude as, or much shorter than, the duration of the experiment. On the other hand, in the thermodynamic limit t_R becomes infinite—which would be acceptable only if t_R were much longer than the duration of the experiment.

The fact that the thermodynamic limit is not, in this respect, a valid approximation for most systems of interest is crucial, since the assumption that nothing ever returns from the boundaries of the system introduces a trivial form of irreversibility into the problem. This form of irreversibility is seen in the radiative loss of energy by a star. Since there are no mirrors to reflect the radiation back into the star, the process is irreversible. However, this form of irreversibility does not contribute to the explanation of the observed approach to equilibrium in a finite system.

The trivial form of irreversibility is not limited to classical mechanics. In quantum mechanics it corresponds to the transition from a discrete energy spectrum to a continuous one. The wave functions for a continuous spectrum have the character of traveling waves and describe particles or correlations that can simply go away.

To clarify the distinction involved, consider the propagation of sound waves in a gas. If the gas is originally in equilibrium and a disturbance is made at some point, sound waves will be created. Even if these sound waves are not damped, they will spread out and diminish in amplitude. In the thermodynamic limit they will never return to the point of origin and we have found a form of irreversibility. On the other hand, if a spherical wall is built about the point of origin to create a finite system, the sound waves will be reflected back and an echo will be observed Without damping, this echo will be repeated regularly with undiminished intensity; the system will not exhibit irreversibility.

Note that if the sphere contains a real gas (with damping), the echos will become progressively weaker until they are no longer observable. It is this second form of irreversibility which is truly interesting.

Although it is possible that an argument beginning with the thermodynamic limit could clearly distinguish between these two forms of irreversibility, an argument that dealt directly with finite systems would be far more satisfactory.[4]

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