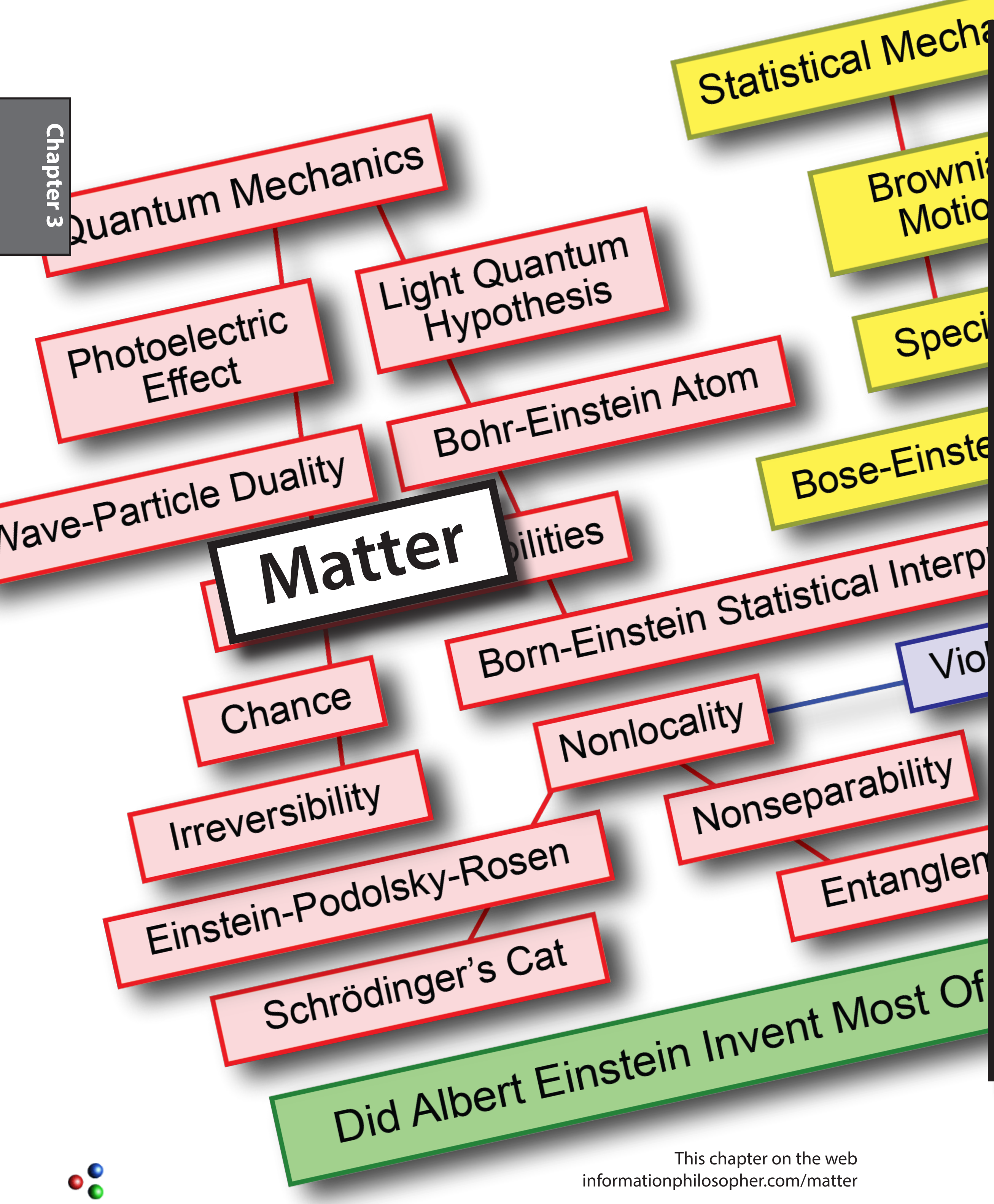

This chapter on the web
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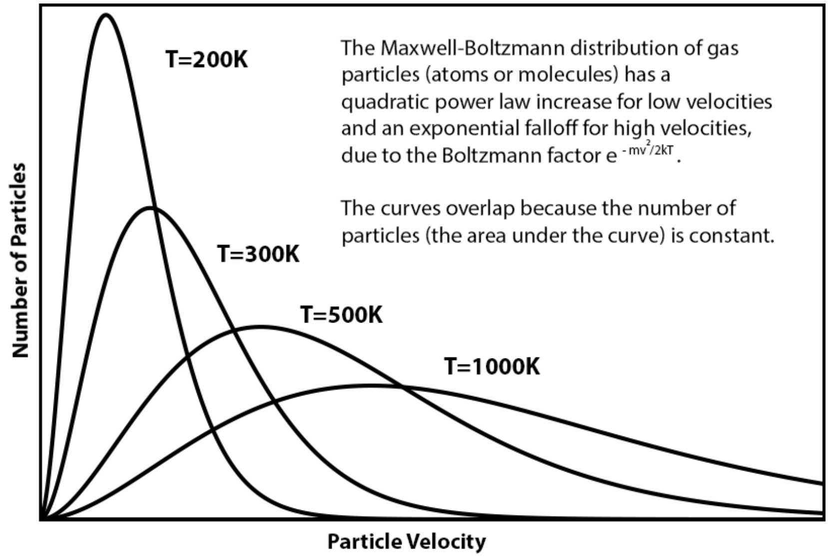
Matter

James Clerk Maxwell and Ludwig Boltzmann were atomists who accepted the idea that the apparently continuous pressure of a gas on the walls of its container is caused by a number of atomic collisions so vast that the individual discrete bumps against the walls are simply not detectable.

Maxwell's great contribution to the kinetic theory of gases was to find the velocity (or energy) distribution of the gas particles. From simple considerations of symmetry and the assumption that motions in the y and z directions are not dependent on motions in the x direction, Maxwell in 1860 showed that velocities are distributed according to the same normal distribution as the "law of errors" found in games of chance. Boltzmann in 1866 derived Maxwell's velocity distribution dynamically, putting it on a firmer ground than Maxwell.



The Maxwell-Boltzmann distribution of gas particles (atoms or molecules) has a quadratic power law increase for low velocities and an exponential falloff for high velocities, due to the Boltzmann factor $e^{-mv^2/2kT}$.

The curves overlap because the number of particles (the area under the curve) is constant.

Maxwell derived his velocity distribution law using math that he found in a review of Adolph Quételet's work on social statistics, but he did not accept the conclusion of Quételet and

Thomas Henry Buckle that the normal distribution seen in large numbers of random events implies that they are *determined*.[1]

Maxwell's criticism of his English colleague Buckle was clear.

> We thus meet with a new kind of regularity — the regularity of averages — a regularity which when we are dealing with millions of millions of individuals is so unvarying that we are almost in danger of confounding it with absolute uniformity.
>
> Laplace in his theory of Probability has given many examples of this kind of statistical regularity and has shown how this regularity is consistent with the utmost irregularity among the individual instances which are enumerated in making up the results. In the hands of Mr Buckle facts of the same kind were brought forward as instances of the unalterable character of natural laws. But the stability of the averages of large numbers of variable events must be carefully distinguished from that absolute uniformity of sequence according to which we suppose that every individual event is *determined* by its antecedents.[2]

Six years after his derivation of the velocity distribution from classical dynamics, Boltzmann found a mathematical expression he called *H* that appears to decrease as particle collisions occur. He identified it as the negative of the thermodynamic entropy that always increases according to the second law of thermodynamics.

In 1874, Boltzmann's mentor Josef Loschmidt criticized his younger colleague's attempt to derive from classical dynamics the increasing entropy required by the second law of thermodynamics. Loschmidt's criticism was based on the simple idea that the laws of classical dynamics are time reversible. Consequently, if we just turn the time around, the time evolution of the system should lead to decreasing entropy.

Of course we cannot turn time around, but a classical dynamical system will evolve in reverse if all the particles could have their velocities exactly reversed. Apart from the practical impossibility of doing this, Loschmidt had showed that systems could exist for which the entropy should decrease instead of increasing. This is called Loschmidt's reversibility objection or "Loschmidt's paradox."

It is also known as the problem of *microscopic reversibility*. How can the macroscopic entropy be irreversibly increasing when microscopic collisions are time reversible?

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[1] See chapter 2 for such arguments beginning with Immanuel Kant.

[2] Draft Lecture on *Molecules*, 1874 (our italics)

Maxwell too was critical of Boltzmann's 1872 dynamical result based on Newton's deterministic laws of motion. The kinetic theory of gases must be purely *statistical*, said Maxwell.

In 1877, Boltzmann followed Maxwell's advice. He counted the number of ways *W* that *N* particles can be distributed among the available cells of "phase-space," a product of ordinary coordinate space and "momentum space."

Boltzmann showed that some distributions of particles are highly improbable, like all the balls in our probability machine landing in one of the side bins. In nature, he said, the tendency of transformations is always to go from less probable to more probable states.[3]

There are simply many more ways to distribute particles randomly among cells than to distribute them unevenly. Boltzmann counted each unique distribution or arrangement of particles as a "microstate" of the system. Arguing from a principle of indifference, he assumed that all microstates are equally probable, since we have no reasons for any differences.

Boltzmann then gathered together microstates that produce similar macroscopic descriptions into "macrostates." For example, having all the particles in a single cell in a corner of a container would be a macrostate with a single microstate, and thus minimum entropy. Boltzmann's idea is that macrostates with few microstates will evolve statistically to macrostates with large numbers of microstates. For example, taking the top off a bottle of perfume will allow the molecules to expand into the room and never return.

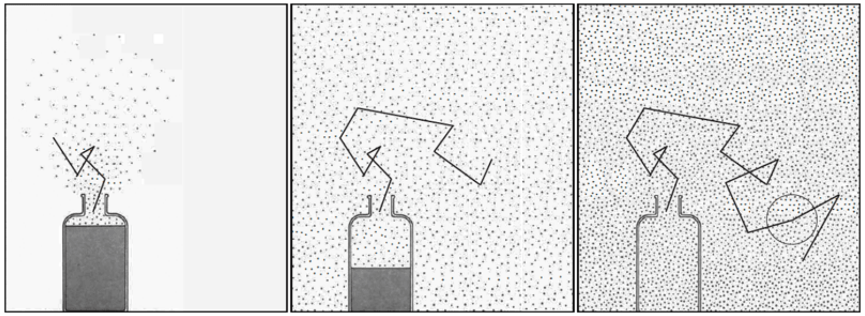

Figure 3-3. Entropy increases when the number of possible microstates W increases. The likelihood of all the molecules returning to the bottle is vanishingly small.

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[3] Boltzmann, 2011, p.74

In the mid 1890's, some British scientists suggested that there must be some low-level mechanism maintaining what Boltzmann had called "molecular chaos" or "molecular disorder." Since classical microscopic dynamical laws of physics are time reversible, collisions between material particles can not explain the *macroscopic* irreversibility seen in classical thermodynamics and in the statistical mechanical explanations developed by Boltzmann.

Boltzmann himself did not take the need for microscopic irreversibility very seriously, because even his classical dynamical analysis showed that collisions quickly randomize a large number of gas particles and his calculations indicated it would be astronomical times before any departure from randomness would return.

For Boltzmann, microscopic irreversibility is needed only to defeat the Loschmidt paradox. See chapter 12.

Boltzmann's Philosophy

In his 1895 *Lectures on Gas Theory*, read by Albert Einstein as a student, Boltzmann raised questions about the continuum and its representation by partial differential equations, which were to be questions Einstein struggled with all his life. Boltzmann wrote,

> Whence comes the ancient view, that the body does not fill space continuously in the mathematical sense, but rather it consists of discrete molecules, unobservable because of their small size. For this view there are philosophical reasons. An actual continuum must consist of an infinite number of parts; but an infinite number is undefinable. Furthermore, in assuming a continuum one must take the partial differential equations for the properties themselves as initially given. However, it is desirable to distinguish the partial differential equations, which can be subjected to empirical tests, from their mechanical foundations (as Hertz emphasized in particular for the theory of electricity). Thus the mechanical foundations of the partial differential equations, when based on the coming and going of smaller particles, with restricted average values, gain greatly in plausibility; and up to now no other mechanical explanation of natural phenomena except atomism has been successful...
>
> Once one concedes that the appearance of a continuum is more clearly understood by assuming the presence of a large number of adjacent discrete particles, assumed to obey the laws of mechanics, then he is led to the further assumption that heat is a permanent motion of molecules. Then these must be held in their relative positions by forces, whose origin one can imagine if he wishes. But all forces that act on the visible body but not equally on all the molecules must produce motion of the molecules relative to each other, and because of the indestructibility of kinetic energy these motions cannot stop but must continue indefinitely...
>
> We do not know the nature of the force that holds the molecules of a solid body in their relative positions, whether it is action at a distance or is transmitted through a medium, and we do not know how it is affected by thermal motion. Since it resists compression as much as it resists dilatation, we can obviously get a rather rough picture by assuming that in a solid body each molecule has a rest position...
>
> If each molecule vibrates around a fixed rest position, the body will have a fixed form; it is in the solid state of aggregation...
>
> However, when the thermal motion becomes more rapid, one gets to the point where a molecule can squeeze between its two neighbors... It will no longer then be pulled back to its old rest position... When this happens to many molecules, they will crawl among each other like earthworms, and the body is molten.
>
> In any case, one will allow that when the motions of the molecules increase beyond a definite limit, individual molecules on the surface of the body can be torn off and must fly out freely into space; the body evaporates.
>
> A sufficiently large enclosed space, in which only such freely moving molecules are found, provides a picture of a gas. If no external forces act on the molecules, these move most of the time like bullets shot from guns in straight lines with constant velocity. Only when a molecule passes very near to another one, or to the wall of the vessel, does it deviate from its rectilinear path. The pressure of the gas is interpreted as the action of these molecules against the wall of the container. [4]

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[4] Boltzmann, 2011 *§1, p.27*