

This single principle combines the two basic axioms of physical statistics:  $P \propto \Omega$  and  $S = k \ln \Omega$ , where  $\Omega$  is the thermodynamic probability (statistical weight) of a macrostate which counts the number of microstates associated with the macrostate. Statistically,  $P \propto \Omega$  states that each accessible microstate of an isolated system in equilibrium is equally probable (fundamental postulate).<sup>1</sup> Dynamically,  $P \propto \Omega$  states that the fraction of time spent in a macrostate is equal to the fraction of microstates in state (phase) space that comprise the macrostate (ergodic hypothesis).<sup>2</sup> In this sense, the probability of a state,  $P$ , is a dynamical object, equal to the fraction of time spent in the state. The statistical motion of a system, as defined by this time spent in states, is the microscopic dynamical information that is relevant to thermodynamics. Although Boltzmann discovered the connection between  $S$  and  $\Omega$ , Planck and Einstein made the relation precise. This principle, in the form  $P/P_m = e^{\Delta S/k}$ , played a prominent role in the formulation and application of statistical mechanics by Planck<sup>3</sup> and Einstein.<sup>4</sup>

$F = ma$  is the equation of motion for a mechanical system.  $e^{\Delta S/k} = P/P_m$  is the equation of motion for a thermodynamical system. I make this claim in the sense that  $e^{\Delta S/k} = P/P_m$  is what remains after  $F = ma$  is averaged over the microscopic degrees of freedom in the many-particle system. Just as the mechanical force ( $F$ ) determines the dynamical motion ( $a$ ), the "thermodynamical force" ( $\Delta S$ ) determines the statistical motion ( $P$ ). In other words, the behavior of the microscopic world, where forces cause the temporal evolution of the states, gets translated into the macroscopic world as entropy changes driving the probability of the states. The large value of the universal "thermodynamic inertia" ( $1/k$ ) makes it difficult for a given thermodynamic force ( $\Delta S$ ) to change the natural state of maximum probability, just as a large mechanical inertia ( $m$ ) makes it difficult for a given force ( $F$ ) to change the natural state of constant velocity. In a world where the thermodynamic mass is infinitely large ( $k = 0$ ), the statistical fluctuations are completely suppressed and the system remains "at rest" in the most probable state. Thus there is a conceptual similarity between the statistical mechanical equation of motion,  $dS = kd(\ln P)$ , and the classical mechanical equation of motion,  $F dt = m dv$ .

It is instructive to push this analogy further. The essence of classical mechanics is the general dynamical law  $F = ma$ , together with the specific laws of force ( $F$ ) that characterize the system–environment interactions in terms of a set of mechanical variables (mass  $m$ , charge  $q$ , position  $r$ , velocity  $v$ , etc.). The essence of statistical mechanics is the general statistical/dynamical law  $e^{\Delta S/k} = P/P_m$ , together with the specific laws of thermodynamic force ( $\Delta S$ ) that characterize the system–environment interactions in terms of a set of thermodynamic variables (temperature  $T$ , pressure  $p$ , chemical potential  $\mu$ , etc.). The thermodynamic force laws are determined by the conservation of energy:  $dU = TdS - pdV + \mu dN$ . This energy equation determines the vital entropy change,  $dS = (dU + pdV - \mu dN)/T$ , that is needed to implement the fundamental principle,  $e^{\Delta S/k} = P/P_m$ . Thus one can see explicitly how the interactions ( $dU, dV, dN$ ) determine the force ( $\Delta S$ ), which determines the motion ( $P$ ). Gradients in temperature, pressure, and chemical potential are thermodynamic forces that move energy, volume, and matter, respectively. The ubiquitous microcanonical, canonical (Boltzmann) and grand canonical (Gibbs) probability distributions are merely special cases of  $P = e^{\Delta S/k} P_m$  applied to a

system and an environment that are in no interaction, in thermal interaction, and in diffusive interaction, respectively.

In summary, I propose that the "equation of motion" of statistical mechanics, in the form  $e^{\Delta S/k} = P/P_m$ , be adopted as the central organizing principle for thermal and statistical physics. Together with the law of "thermodynamic force,"  $dS = (dU + pdV - \mu dN)/T$ , this principle contains complete information on the statistical motion of a system through state space via the probability of states. The entire subject of equilibrium statistical mechanics and thermodynamics logically unfolds from these physical statistics of the states.

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<sup>1</sup>F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), Sec. 2.3.

<sup>2</sup>R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford U.P., London, 1962), Sec. 25.

<sup>3</sup>Max Planck, *Theory of Heat* (Macmillan, London, 1932), Part Four, Chap. I.

<sup>4</sup>A. Einstein, "On the general molecular theory of heat," *Ann. Phys.* **14**, 354–362 (1904).

**Answer to Question #24 ["Can an electron be at rest?," Terrence P. Toepker, *Am. J. Phys.* **63** (9), 777 (1995)]**

Classically, a particle is at rest (in some frame) when its velocity and momentum vanish. In quantum mechanics simply requiring the expectation value of momentum to be zero implies only that the particle's average velocity is zero. Something closer to the classical meaning of "rest" is achieved only when one requires that the expectation value of the square of the velocity be vanishingly small as well. As indicated in the statement of the Question, the uncertainty principle then tells us that this condition can only be achieved if the particle is in an arbitrarily large box.

Consider the recent example of trapped <sup>87</sup>Rb atoms that formed a Bose–Einstein condensate [Anderson *et al.*, *Science* **269**, 198 (1995)]. Those atoms were most nearly at rest for any particles studied to date. The trap size was about 0.1 mm so the corresponding rms atomic velocity was  $\hbar/m\Delta x \approx 1$  cm/s. While this might seem high by classical standards, it corresponds to a temperature of only a few  $\times 10^{-7}$  K and is a remarkable achievement.

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**Answer to Question #24 ["Can an electron be at rest?," Terrence P. Toepker, *Am. J. Phys.* **63**(9), 777 (1995)]**

The question of T. P. Toepker (TPT) deals with one of the unsolved problems in the foundations of quantum mechanics. A definite answer cannot be given, but I will present some alternative opinions tied to different interpretations of quantum mechanics, trying (and failing) to be unbiased.

The strict orthodox Copenhagen Interpretation, close to a positivistic philosophy, would say that the question is illegal.