1 Einstein's Miraculous Argument of 1905: The Thermodynamic Grounding of Light Quanta

JOHN D. NORTON

A major part of Einstein's 1905 light quantum paper is devoted to arguing that high frequency heat radiation bears the characteristic signature of a microscopic energy distribution of independent, spatially localized components. The content of his light quantum proposal was precarious in that it contradicted the great achievement of nineteenth century physics, the wave theory of light and its accommodation in electrodynamics. However the methods used to arrive at it were both secure and familiar to Einstein in 1905. A mainstay of Einstein's research in statistical physics, extending to his earliest publications of 1901 and 1902, had been the inferring of the microscopic constitution of systems from their macroscopic properties. In his statistical work of 1905, Einstein dealt with several thermal systems consisting of many, independent, spatially localized components. They were the dilute sugar solutions of his doctoral dissertation and suspended particles of his Brownian motion paper.[1]

1.1 Introduction

The year 1905 is now commonly known as Einstein's "year of miracles." In it, in a series of extraordinary papers, the 26-year-old clerk in the Bern patent office redirected the course of physics. Those five papers were, in order of their dates of submission and publication:

- Light quantum ("photoelectric effect") paper (Einstein, 1905a). Einstein inferred from the thermal properties of high frequency heat radiation that it behaves thermodynamically as if constituted of spatially localized, independent quanta of energy.

- Einstein's doctoral dissertation (Einstein, 1905b). Einstein used known physical properties of sugar solutions (viscosity, diffusion) to determine the size of sugar molecules.

- Brownian motion paper (Einstein, 1905c). Einstein predicted that the thermal energy of small particles would manifest as a jiggling motion, visible under the microscope and providing the most direct support then available for the molecular-kinetic approach to thermal systems.

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- Special relativity (Einstein, 1905d). Einstein urged that maintaining the principle of relativity in electrodynamics requires a new theory of space and time.

- $E = mc^2$ (Einstein, 1905e). Einstein showed that changing the energy E of a body changes its inertia m in accord with $E = mc^2$.

In a letter of May 2005, Einstein described the first four of these papers to his friend Conrad Habicht. It is striking and noteworthy that Einstein singles out the first paper, the light quantum paper, for an extraordinary description "The [first] paper deals with radiation and the energy properties of light and is very revolutionary,..." (*Papers*, Vol. 5, Doc. 27)

It is not hard to see why Einstein would single out his light quantum paper in this way—and that remains true if we include consideration of the later $E = mc^2$ paper, which had not been conceived at the time of Einstein's May letter. All but the light quantum paper develop or complete programs of research of nineteenth century physics, sometimes in quite inspired ways. The two statistical papers, the dissertation and the Brownian motion paper, advance decisively a program of research in thermal systems developed by Maxwell, Boltzmann and others in the nineteenth century, the molecular kinetic theory of heat. The special relativity paper establishes the real significance of the Lorentz covariance of Maxwell's electrodynamics, that it betokened a new theory of space and time. Finally, the $E = mc^2$ paper took a result from electrodynamics, that light energy has momentum, and used the principle of relativity to extend it to all forms of energy.

The light quantum paper was different. The signal achievements of nineteenth century physics were: the wave theory of light and the recognition that Newton's authoritative corpuscular theory fails; Maxwell's electrodynamics and its development and perfection by Hertz, Lorentz and others; and the synthesis of the two in the single luminous idea that light waves just are electromagnetic waves. Einstein's light quantum paper threatened this great synthesis in its fundamentals. Light, Einstein now asserted, did not always behave as a wave. Sometimes it behaved as if its energy was localized into independent points in space. Indeed with this idea of the light quantum, Einstein initiated a reappraisal of the physical constitution of light that is not entirely resolved over a hundred years later.

My concern in this paper is to answer the question of how even an Einstein could have the courage to propose this revolutionary notion of the light quantum. My analysis will depend on distinguishing the *content* of the light quantum hypothesis from the *methods* Einstein used to arrive at it. The content of Einstein's discovery was quite unanticipated: it asserted that high frequency light energy exists in independent, spatially localized

points. However the *method* of Einstein's discovery was familiar and secure. His research program in statistical physics from his first publication of 1901 returned repeatedly to the question: How can we infer the microscopic properties of matter from its macroscopic properties? For example, the dissertation and Brownian motion paper of 1905 were devoted to analyzing dilute sugar solutions and very small particles suspended in a fluid. That is, they were devoted to studying thermal systems whose statistical constitution was similar to the one Einstein attributed to high frequency light energy, in that they consist of many, independent, spatially localized, points (sugar molecules, small particles). As a result Einstein was adept at dealing with such systems and, most importantly, quite sensitive to how such systems appear macroscopically.

My goal here is not to give a fine-grained reconstruction of Einstein's pathway to the light quantum. Many pathways are compatible with the analysis I shall give. My goal is to show that, if we locate Einstein's light quantum paper against the background of electrodynamic theory, its claims are so far beyond bold as to be foolhardy. However, if we locate Einstein's light quantum paper against the background of his work in statistical physics, its methods are an inspired variation of ones repeatedly used and proven effective in other contexts on very similar problems.

The miraculous argument and its similarity to Einstein's other projects from that time will be outlined in Section 4.2 and 4.3. In Section 4.4, I will note that the ideal gas law is a more familiar signature of the microscopic constitution Einstein inferred for radiation; and in Section 4.5 I will explain why I believe Einstein did not use it in his argument. Finally, in Section 4.6, I will review a remarkably simple and much repeated argument that Einstein advanced in his light quantum paper for what he named Boltzmann's principle: "$S = k \log W$." I will argue that the maddening imprecision of the argument was needed because it was to be applied to systems of light quanta whose full properties were correspondingly imprecisely known.

1.2 The Miraculous Argument

Einstein's light quantum paper (1905a) has nine parts. The last three pertain to empirical vindications of the light quantum hypothesis. Einstein's famous analysis of the photoelectric effect appears in the eighth part only ("On the generation of cathode rays by illumination of solid bodies"). It has such a minor role in the paper that it seems inappropriate to give the paper the moniker, "the photoelectric effect paper." The bulk of the paper, from the first to the sixth sections, is largely devoted to setting up and stating just one argument that comes to fruition in sixth section ("Interpretation of the expression for the dependence of the entropy of monochromatic radiation on volume according to Boltzmann's Principle"). There Einstein infers that the measured thermo-dynamic properties of high frequency heat radiation carry the distinctive signature of independent, spatially localized points. This argument is, in my view, the most inspired of all Einstein's achievements of 1905 and, for this reason, I have chosen to call it "the miraculous argument."

There were two steps in the argument. The first appeared in the fifth section ("Molecular-theoretical investigation of the dependence of the entropy of gases and dilute solutions on the volume"). It laid out a simple piece of statistical physics. Einstein considered a system consisting of n independently moving points in a volume V_0 of

space. It followed immediately from the independence of the points that the probability W that all n points are located in some subvolume V is just

$$W = \left(\frac{V}{V_0}\right)^n \tag{1.1}$$

In that same section, Einstein had already presented a brief argument for what he called "Boltzmann's Principle" (See Section 4.6 below.) That principle

$$S = k \log W \tag{1.2}$$

used Boltzmann's constant k to make a connection between the probabilities W of microstates and their corresponding macroscopic entropies S. Applying (4.2) to (4.1), Einstein inferred that the entropy change associated with the volume change of (4.1) is

$$S - S_0 = kn \log \left(\frac{V}{V_0}\right) \tag{1.3}$$

In a footnote, Einstein then used standard thermodynamic relations to deduce from (4.3) that the n points would exert a pressure P at temperature T that conforms to the ideal gas law

$$PV = nkT \tag{1.4}$$

The obvious application of these results is to the n molecules of an ideal gas, which is thereby deduced to conform to the ideal gas law (4.4). The probability W of (4.1) is the probability that the gas spontaneously fluctuates to a smaller volume V in the larger volume V_0. Unless V coincides almost exactly with V_0, the probability of these fluctuations for macroscopically sized samples of gas is exceedingly small.

Systems governed by the analysis could be quite different from an ideal gas, however. All that is needed is that the components of the system are independent, spatially localized points. That would be true of molecules of sugar, say, in a dilute solution; or a few, widely spaced small particles suspended in a liquid. All that mattered for the analysis was that these molecules or particles do not interact with each other. That they are in continuous interaction with the surrounding solvent is irrelevant to the deduction of (4.3) and (4.4). As a result it follows immediately that the ideal gas law obtains for the osmotic pressure exerted by a dilute solution. That is true, even though microscopically the solute molecules do *not* move according to the familiar picture of the ideal gas of introductory text books: long periods of free, inertial motion, interrupted briefly by collisions.

Thus far, the analysis was a simple and vivid illustration of basic ideas in statistical physics. The second step of the argument was developed in the following section and was anything but standard. Einstein returned to the measured results concerning heat radiation that he had reviewed in earlier sections. From these results, he inferred the volume dependence of the entropy of a quantity of high frequency heat radiation. That is, if a quantity of heat radiation of fixed energy E and definite frequency ν occupies volume V or V_0, then the corresponding entropies S and S_0 are related by[2]

$$S - S_0 = k \left(\frac{E}{h\nu}\right) \log \left(\frac{V}{V_0}\right) \tag{1.5}$$

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[2]I have modified the expression of Einstein's formula notationally by replacing a constellation of constants of Einstein's formula by the modern h.

Einstein then used Boltzmann's principle (4.2) to invert the inference from (4.1) to (4.3). It now followed that there is a probability W satisfying

$$W = \left(\frac{V}{V_0}\right)^{\frac{E}{h\nu}} \tag{1.6}$$

Einstein immediately noted that this probability was just like the probability of the process of spontaneous volume fluctuations of n independent, spatially localized points, where

$$n = \frac{E}{h\nu} \tag{1.7}$$

That is, it was as *if* the energy E of the heat radiation had been divided into n independently moving, spatially localized points of size $h\nu$. Preserving the "as if" qualification, Einstein then gave the most cautious and complete statement of the light quantum hypothesis of the paper:

> Monochromatic radiation of low density behaves—as long as Wien's radiation formula is valid [i.e. at high values of frequency/temperature]—in a thermodynamic sense, as if it consisted of mutually independent energy quanta of magnitude [$h\nu$].

The "as if" qualification was only a temporary caution. It was dropped in other statements of his conclusion elsewhere in the paper, now taken against the full background of the other experimental results offered as vindicating the light quantum hypothesis.[3]

While Einstein passed immediately from the formula (4.6) to the light quantum hypothesis, two tacit assumptions were needed for the inference. First, the entropies S and S_0 of expression (4.5) were deduced for systems of radiation in equilibrium. Einstein now tacitly assumed that that the change of entropy (4.5) would obtain also for transitions to non-equilbrium states such as when a volume V_0 of heat radiation fluctuates to a non-equilibrium state with a smaller volume V.[4]

Second, Einstein tacitly assumed that just such a fluctuation process was possible in which the volume V_0 would spontaneously contract to the small V in such a way that the system's energy E and high frequency ν would remain unchanged. The constancy of the energy E was assured by the conservation of energy for an isolated system. However it is not so clear what justifies the assumption of the constancy of the frequency.

This last assumption can easily pass unnoticed if one already has in mind that the system of radiation consists of many non-interacting quanta, each with a characteristic frequency parameter n. But having that in mind is to anticipate the conclusion, whereas the goal is to infer this conclusion. Minimally one can say that the assumption of constancy of frequency entails the evidence of the observed entropy change and, by virtue of that entailment, the constancy is inductively supported by the evidence. What

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[3]For example, in the introduction to the paper Einstein writes that the full constellation of evidence assembled in the paper "seems to be understood better through the assumption that the energy of light is distributed discontinuously in space" and that light propagating from a point source "consists of a finite number of energy quanta, that are localized at points in space, move without dividing and can only be absorbed or produced as a whole."

[4]For further discussion of this assumption, see *Norton* (2006, p. 87, n. 15), where it is suggested that the essential condition is that the descriptions of the equilibrium and non-equilibrium macrostates states delimits the same volume of phase space.

would be better is if there was independent support for the assumption. That may be hard to secure. The dynamical laws of the system govern how its frequency will change over time. The whole point of Einstein's argument is to establish that these dynamical laws are not Maxwell's equations; or perhaps that these equations hold at best for the averages of quantities.[5] The fluctuation process is a deviation from average behavior, so we do not know what those dynamical laws are. The presumption that these laws involve quanta that preserve their frequency parameters over time if they are non-interacting is, once again, to anticipate the conclusion sought.

1.3 A Familiar Project

What Einstein achieved with his miraculous argument was an inference from the macroscopic properties (the volume dependence of entropy of high frequency thermal radiation) of a thermal system to it microscopic constitution (independent, spatially localized energy quanta). This sort of project was quite familiar to Einstein. It has been the repeated theme of much of his work in statistical physical of 1905 and earlier. His doctoral dissertation (Einstein 1905b) was devoted to inferring from the macroscopic properties of dilute sugar solutions (viscosity, diffusion) to an essential element of their microscopic constitution (size of sugar molecules). In his Brownian motion paper (Einstein 1905c), he established that the predicted[6], microscopically visible motions of suspended particles result from collisions with moving water molecules and thus would provide a visible manifestation of these last motions. The profound importance of this result was that Einstein had found an effect that could not be treated by equilibrium thermodynamics. Thermodynamicists could no longer ignore the molecular kinetic program if they were to account for the visible motions of suspended particles Einstein now predicted.

The overall project was the same in Einstein's first two publications (Einstein 1901, 1902). These papers now attract little attention in history of science. That conforms with Einstein's own judgment that they are "worthless beginner's works," as expressed to Johannes Stark in a letter of December 7, 1907 (*Papers*, Vol. 5, Doc. 66). A result of this neglect is that it is easy to overlook the continuity in Einstein's projects that extends back to these earliest papers. The goal of these early papers was to develop an hypothesis on the forces between molecules. Einstein had hypothesized that the force between two molecules separated by a distance r is generated by a potential P satisfying

$$P = P_\infty - c_1 c_2 \varphi(r) \tag{1.8}$$

where P_∞ is the potential when the molecules are infinitely far apart, constants c_1 and c_2 are characteristic of the two molecules and $\varphi(r)$ is a universal function. Einstein's goal in these papers was to test this hypothesis and to determine values of the constants $c_1 c_2$. In the first of these two papers (1901), Einstein sought to infer these microscopic quantities from macroscopic properties of capillarity. In the second (1902), Einstein

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[5]This possibility is suggested by Einstein's remark in the introduction to the paper that optical experiments on diffraction, reflection, refraction, dispersion, etc. pertain only to the time averages of quantities.

[6]Einstein (1905c) suggested in the introduction to the paper that these motions may be Brownian motion but lamented that the data available to him on Brownian motion was too imprecise for him to know.

replaced macroscopic properties of capillarity with electrochemical potentials known through investigations in electrolysis.

Much of Einstein's earlier and contemporary work was devoted to the project of inferring microscopic constitutions from macroscopic properties. So he had become familiar and quite adept at this project. There was a closer similarity to the project of Einstein's light quantum proposal, as we shall see in the following section.

1.4 Signatures of Many, Independent, Spatially Localized Points

The central idea of Einstein's miraculous argument can be encapsulated in a single, powerful idea. Sometimes it is possible to see a signature of the microscopic constitution of a thermal system in its macroscopic thermodynamic properties. Einstein had identified just such a signature for systems consisting of independent, spatially localized components. That signature is given as the dependence of entropy on the logarithm of volume as expressed in equation (4.3). If that dependency can be identified, then we have a strong indication that the system consists of independent, spatially localized components; the number of components n can be read directly from the constant of proportionality of (4.3), which is just kn.

There was, it turns out, a much more familiar (but slightly less powerful) signature of this same microscopic constitution. It is the ideal gas law itself. If one has a system of many, independently moving points, microscopically speaking, they will tend to scatter due to their random thermal motions. This tendency can be redescribed macroscopically as a pressure exerted by the system. It is the ordinary pressure of an ideal gas or the osmotic pressure of dilute solutions.

Well before 1905, it was well known that this relationship could be used as a bridge to pass from the macroscopic observables of a system to its microscopic constitution. To mention one important example, Arrhenius (1887) had used it as a means of inferring the degree of dissociation of solutes in solution. Take, for example, a binary solute. If it is fully dissociated in solution, there will be twice as many components in the solution as there would be if the solute were completely undissociated. That means the osmotic pressure of the fully dissociated solute would be twice that of a completely undissociated solution. As a result, the degree of dissociation of the solute could be determined simply by measuring the osmotic pressure and determining its location between the two extremes.

This ideal gas law and its microscopic underpinnings was an essential component of Einstein's analysis of the diffusion of sugar in his dissertation and of the scattering of small particles in the Brownian motion paper. He used it to deduce an equation important to the analysis of both papers. That equation related the diffusion coefficient D of systems of sugar molecules or suspended particles, a macroscopic measure of their tendency to scatter, with microscopic quantities, including the radius S of the molecule or particle[7]

$$D = \left(\frac{RT}{6\pi\eta}\right)\left(\frac{1}{NS}\right) \tag{1.9}$$

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[7] N is Loschmidt's (Avogadro's) number; R is the ideal gas constant; η is the viscosity of the suspending fluid.

This equation was deduced by considering a solution or system of suspended particles in a gravitational field. Gravity would lead the solute and small particles to fall at a rate limited by the viscosity of the fluid and expressed by Stokes law. Osmotic pressure, as given by the ideal gas law, would scatter the solutes and small particles upward. Since the system is at equilibrium, the two motions must cancel on average. Setting them equal yields (4.9).

The deduction of this result depended upon the ideal gas law holding both for the osmotic pressure of a solute and for the pressure used to model the tendency of suspended particles to scatter. While the former conformity to the ideal gas law was widely accepted, the latter was not. For it suggested that the statistical methods of the molecular kinetic approach should apply to small particles visible under the microscope as well. So, in the second section of the Brownian motion paper, Einstein gave a long and careful demonstration of just how little was needed to deduce the ideal gas law. Essentially one needed only to assume that the components of the relevant system did not interact with each other.[8] Small particles suspended in a fluid satisfied this condition if they are spaced widely enough. All that remained was to use the formalism of statistical physics to re-express this fact about the components in macroscopic terms to recover the ideal gas law.

A simpler version of the inference—not given by Einstein—shows just how direct the connection was. Consider a thermal system of independent, spatially localized components (e.g. solute molecules or small particles suspended in a fluid) in a gravitational field.[9] This system is governed by Boltzmann's distribution. So the probability $P(h)$ that a given component is located at height h is

$$P(h) = constant \ e^{\frac{-E(h)}{kT}} \tag{1.10}$$

The essential fact of the independence of the components is expressed in this formula through the fact that the energy $E(h)$ of each component is a function of height h only.[10] That is, it is independent of the positions of the other components. It now follows immediately that the density ρ of components at height h in relation to its density ρ_0 at height $h = 0$ is

$$\rho = \rho_0 e^{\frac{-E(h)}{kT}}$$

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[8]This fact is quite remarkable. That sugar molecules in a dilute solution will be in constant interaction with the molecules of water of the solvent does not affect the recovery of the ideal gas law for the sugar's osmotic pressure. All that matters is that the sugar molecules do not interact with each other, a condition enforced by the diluteness of the solution.

[9]The standard technique for introducing osmotic pressure in the literature had been through the force exerted by some species of a solute on a semi-permeably membrane, that is, a membrane permeable to everything but the molecules of that species of solute. In his (1902), Einstein had expressed doubts over whether such membranes are realistic. With great care, he proposed that osmotic pressures are better analyzed by equilibration with conservative fields that would act differentially on the different species of solute molecules. This technique enables the greatly simplified and generalized derivation of the ideal gas law presented here. Einstein introduced the technique casually in both his dissertation and his Brownian motion paper without giving a citation to his earlier, careful analysis of it. This is another example of Einstein's laxity in citing his sources, yet in this case it was his own earlier work that was obscured.

[10]It is assumed that the total energy is a sum $E = E(h) + E_{KE}$, where E_{KE} is the component's kinetic energy. The kinetic energy will contribute a term to (4.10) that is absorbed into the constant

The density gradient due to gravitational field can be found by differentiating this expression with respect to h

$$\frac{\mathrm{d}\rho}{\mathrm{d}h} = -\frac{1}{kT}\frac{\mathrm{d}E}{\mathrm{d}h}\rho$$

This equilibrium density gradient arises from a balancing of two forces. The first is the gravitational force density

$$f = -\frac{\mathrm{d}E}{\mathrm{d}h}\rho$$

acting on the components in the downward direction. It is balanced by the pressure P that arises from the tendency of the components to scatter. Components will be accelerated whenever there are neighboring regions of different pressure. The resulting force f is given by the pressure gradient

$$f = \frac{\mathrm{d}P}{\mathrm{d}h}$$

Combining, the expression for the density gradient becomes

$$\frac{\mathrm{d}\rho}{\mathrm{d}h} = -\frac{1}{kT}\frac{\mathrm{d}E}{\mathrm{d}h}\rho = \frac{1}{kT}f = \frac{1}{kT}\frac{\mathrm{d}P}{\mathrm{d}h}$$

Rearranging the terms, we recover

$$\frac{\mathrm{d}}{\mathrm{d}h}(P - \rho kT) = 0$$

Integrating with the boundary condition that $P = 0$ when $\rho = 0$ yields a local form of the ideal gas law

$$P = \rho kT$$

When the component distribution is sufficiently homogeneous that it can be represented as n components spread uniformly over a volume V, we have $\rho = n/V$ and the ideal gas law adopts its extended form

$$PV = nkT$$

This demonstration shows clearly that the ideal gas law is little more than a macroscopic re-expression of the microscopic fact of independence of spatially localized components. Its simplicity strongly suggests that the inference may be inverted: when we have a system of components obeying the ideal gas law, we can infer that they are independent, spatially localized components. The inference can be so inverted, although the details are a little messy.[11] Thus the ideal gas law can function as a signature of the microscopic constitution of a system, although, as we shall see in the next section, it proves to be a little less revealing than Einstein's entropy-volume relation (4.3).

1.5 Why Didn't Einstein Use the Ideal Gas Law as the Signature?

The results of the last section raise a question. Why did Einstein need to discover a new macroscopic signature of the microscopic constitution of independent, spatially localized

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[11]See *Norton* (2006, Appendix A "The Ideal Gas Law").

components? The ideal gas law is a long-standing, widely appreciated signature of just such a constitution; one that would be understood more easily by his readers of 1905; and one that Einstein was so familiar with, that his other work of 1905 included a thorough analysis of it.

There is one easy answer to the question that does not bear scrutiny. One might imagine that the ideal gas law fails for high frequency heat radiation. For the simplest application of the ideal gas law is to an isothermal expansion of a gas. In such a process the gas pressure P varies inversely with the volume V; this specialization of the ideal gas law is Boyle's law

$$PV = constant \tag{1.11}$$

This result does not obtain for heat radiation, however. It is a familiar property of heat radiation that the pressure P it exerts is a function solely of the energy density u

$$P = \frac{u}{3} \tag{1.12}$$

The energy density u is, in turn, a function of the temperature and frequency only; or it is a function of the temperature only, if we consider full spectrum heat radiation. So, in an isothermal expansion of full spectrum heat radiation, the pressure P will stay constant precisely because the process is isothermal and has a fixed temperature.

This constancy of pressure in an isothermal expansion does not establish the failure of the ideal gas law for heat radiation. The inference to the failure is flawed since it does not take into account an essential disanalogy between ideal gases and heat radiation. For an ideal gas, the number of components, that is, the number of molecules, remains constant during an isothermal expansion. For heat radiation, however, the number of components does not remain constant during an isothermal expansion. Indeed this process will create new quanta. The total energy $E = uV$. Since u stays constant in the process and V increases, it follows that the system's total energy E must increase and, with it, the total number of quanta also increases.[12] This means that the relevant specialization of the ideal gas law to the isothermal expansion of heat radiation is not Boyle's law (4.11), but one that retains dependency on n

$$PV = constant \; n$$

This extended form of Boyle's law obtains for the isothermal expansion of ideal gases and also, as we shall see in a moment, for high frequency heat radiation as well. Where they differ is in how P behaves during the expansion. For an ideal gas, since n is constant, pressure P will decrease in inverse proportion to V. For high frequency heat radiation, the number of quanta n will grow in direct proportion to the volume V; the result is that P remains constant during the process.

So far, we have only seen that consideration of isothermal expansions do not give *prima facie* grounds for expecting the ideal gas law to fail for heat radiation. That does not establish that the ideal gas law does obtain for heat radiation. The ideal gas law does indeed obtain for high frequency heat radiation, although to see it requires a result from Einstein's 1905 light quantum paper. In Section 6 of that paper, Einstein computed

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[12]Contrast this with the familiar property of ideal gases, that their total energy remains constant during an isothermal expansion.

the mean energy of quanta for radiation governed by Wien's distribution law. That law obtains for high frequency radiation, so Einstein's result holds as long as we consider only high frequency radiation. He found that the mean energy of these quanta is $3kT$, so that the energy density $u = 3nkT/V$. Combining this with the expression (4.12) for radiation pressure, we find

$$P = \frac{u}{3} = \frac{(3nkT/V)}{3} = \frac{nkT}{V}$$

which is just the ideal gas law.[13] Now we can return to the question posed at the start of this section. The ideal gas law does obtain for heat radiation and was then a familiar signature of a microscopic constitution of many, independent components. So why didn't Einstein use it in his light quantum paper? Einstein gave no answer to this question. However even a cursory perusal of how the corresponding argument would run shows that it would be quite unconvincing as a means of establishing the existence of quanta. For high frequency radiation governed by Wien's distribution, the energy density u of radiation would conform to the familiar Stefan-Boltzmann law $u = \sigma T^4$. Substituting this into the expression for radiation pressure (4.11) we recover

$$P = \frac{u}{3} = \frac{\sigma T^4}{3} = \left(\frac{\sigma V T^3}{3k}\right) k \frac{T}{V} = \frac{nkT}{V}$$

To complete the argument, we would need to proclaim that the number of quanta can be read from the last equality as

$$n = \frac{\sigma V T^3}{3k}$$

That would be a quite unconvincing proclamation to someone who has no allegiance to the notion of the light quantum and may even have never conceived it. The equality makes clear that the number of quanta will vary in most familiar thermodynamic processes. We see that the number of quanta n will increase in direct proportion to the volume V, as noted before. The number of quanta n will also increase with the cube of temperature. One would be forgiven for thinking that these components are rather unlike the permanent gas molecules, solute molecules and suspended particles of the familiar applications of the ideal gas law. These quanta are a created and destroyed by expansion and compression and by heating and cooling. Indeed, if one is unsure of the number of components in a thermal system, the ideal gas law is not a reliable signature of their constitution. That is, the mere proportionality of PV with kT for some thermal system does not assure us that the constant of proportionality is the number of spatially localized components.[14] However if we know the number of components so that we supply the "n" of $pV = nkT$, the obtaining of the ideal gas law does allow us to infer their independence and spatial localization.

Since Einstein had no independent indication of the number of components in high frequency heat radiation, he needed a different signature; and ideally it would be one that does not draw attention to the tenuous existence of light quanta. Such a signature should be sought in processes that leave the number of quanta fixed. There are very few such

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[13]The ideal gas law also turns out to obtain if we consider a single frequency cut of high frequency heat radiation, although the calculation is more difficult. For details, see *Norton* (2006, p. 91).

[14]For an illustration of how the inference can fail, see *Norton* (2006, p. 77–78)

processes. Heating, cooling and the normal sorts of volume changes all alter the number of quanta. What Einstein managed to locate in the process of volume fluctuations is a process, rare among those treated by the thermodynamics of heat radiation, that turns out not to alter the number of quanta. As a result, it proves especially hospitable to the signature Einstein employed of the dependence of entropy on the logarithm of volume. Moreover he did not need to know in advance how many components comprised the system under investigation. Once the proportionality of entropy and the logarithm of volume was ascertained, the number of components could be read from the constant of proportionality.

Finally, it should be noted that this signature of the dependence of entropy on the logarithm of volume is much harder to see in heat radiation than in the case of ideal gases. In the case of ideal gases, the two states that are related by the probability formula (4.1) can also be connected by an isothermal compression. That means that the dependence of entropy on the logarithm on volume is a familiar result from studies of the processes of equilibrium thermodynamics. That is not the case for heat radiation. Unlike the case of an ideal gas, an isothermal compression of a system of heat radiation will change the system's energy. It follows that this process is not governed by the entropy-volume relation (4.3) that is central to Einstein's argument. More complicated processes, such as the volume fluctuation process Einstein described, are needed to connect the two states.

1.6 Einstein's Demonstration of Boltzmann's Principle

The considerations developed here help us understand the role played by a famous demonstration Einstein included in Section 5 of his light quantum paper. There Einstein sought to lay out a general argument for what he called "Boltzmann's principle," which is expressed in the iconic formula "$S = k \log W$" rendered as (4.2) above.

The argument begins by considering two independent thermal systems with probabilities W_1 and W_2. Because the systems are independent, the probability of the joint system is simply given by the product

$$W = W_1 W_2 \tag{1.13}$$

Now, Einstein continued, entropy S is a function of $\varphi(W)$ of probability and, since entropy is an extensive magnitude, the entropy S of the joint system must be the sum of the entropies S_1 and S_2 of the two component systems

$$S = S_1 + S_2 \tag{1.14}$$

It is a simple problem in functional analysis to verify that the only function $S = \varphi(W)$ satisfying these two conditions (4.13) and (4.14) is

$$S = constant \log W \tag{1.15}$$

where the constant of this relation must be Boltzmann's constant k if the relation is to conform with other results in the kinetic theory of gases.

It is hard not to be dazzled by this argument. It requires only the simplest of analyses to deliver a beautifully simple explication of entropy, the most contentious notion in statistical physics. Yet the argument is also quite maddening. For, in its speedy execution, it passes in silence over a series of important questions:

- What are the probabilities of equation (4.13)? The probability of an outcome has no clear meaning if we do not specify an outcome space and the conditions governing it. We cannot speak without fatal ambiguity of the probability that a coin shows a head if we do not also specify that we have a fair coin with a head on one side and a tail on the other and that it is flipped in a fair toss.

- To arrive at the simple formula (4.15), Einstein must assume that entropy S is a function of probability only. Otherwise the constant of the formula is constant only with respect to probability; we have not ruled out the possibility that it is a function of the system's other properties. How do we know that entropy S is a function of the probability W only, for all thermal systems, not just for kinetic gases?

- Einstein's argument connects only to the thermodynamic notion of entropy in that it is required in (4.14) that the quantity S be an extensive magnitude. It is not shown that the resulting S of $S = k \log W$ coincides with the thermodynamic entropy of the system as specified in the Clausius definition

$$S - S_0 = \int dq_{rev} \frac{1}{T} \tag{1.16}$$

  where S is the entropy of a system with initial entropy S_0 after a reversible process in which quantities of heat qrev are imparted to it at temperature T. At best the argument can establish that, if there is any quantity at all that is a function of probability only that coincides with thermodynamic entropy, then it must be that of (4.15).

Clausius' entropy (4.16) is defined only for equilibrium states. Yet Einstein intends the quantity S of (4.15) to apply to non-equilibrium states such as are produced by fluctuation processes. Does Einstein have an independent standard that authorizes his assigning the term "entropy" to this quantity? Or is it a definition? If it is a definition, why is it appropriate to continue to assume that the extended notion of entropy now being defined should conform to the additive requirement (4.14)? Perhaps a natural, non-equilibrium notion of entropy is non-additive.

My point here is not to deny Einstein's result. In so far as we now have a serviceable explication of entropy in the modern literature, it equates entropy with k times the logarithm of volume in phase space; that is the analog of Einstein's $S = k \log W$. Rather my point is that Einstein's analysis is hasty in the way it suppresses background assumptions and steps needed to complete the argument.

Einstein certainly knew how to give a more precise analysis of entropy in terms of phase space quantities. It was included in his papers prior to 1905 on the foundations of statistical mechanics. Notably Section 6 of Einstein (1903) used Clausius' definition (4.16) of thermodynamic entropy to ground the expression for the canonical entropy of an equilibrium system at temperature T and with mean energy in a phase space with canonical coordinates $p_1, ..., p_n$

$$S = \frac{\bar{E}}{T} + k \log \int e^{(-\frac{E}{kT})} \, dp_1 \dots dp_n \tag{1.17}$$

Indeed this result was not far from Einstein's thoughts in 1905. It is recapitulated, along with the statement of the equations of motion governing the system point of the phase space, in Section 2 of the 1905 Brownian motion paper and forms the basis of Einstein's derivation of the ideal gas law.

So why did Einstein regress from the precision of his 1903 analysis of the canonical entropy formula (4.17) to the ambiguity and incompleteness of his 1905 demonstration of Boltzmann's principle? My conjecture is that Einstein regressed to a less precise analysis because the 1903 analysis required presumptions that he knew were either false for light quanta or at least uncertain; and it did not analyze quite the process at issue in 1905.

To elaborate, the 1903 analysis presumed a fixed number of components, in so far as the number of components in the system is equated with the dimension of the phase space. For the 1903 analysis presumed a phase space with n fixed dimensions and fixed canonical coordinates $p_1, \ldots, p_n$. Einstein's 1905 system, however, had a variable number of components, in that the number of quanta vary in the course of typical thermodynamic processes.

Next, Einstein's 1903 analysis presumed definite, Hamiltonian-like equations of motion. Einstein's analysis 1905 analysis of light quanta had yielded no equations of motion for individual quanta. At best one could guess what they might be in special cases.[15]

Finally, the 1903 analysis connected the entropy of a system at thermal equilibrium with the corresponding phase space quantities. In 1905, Einstein needed more. It was essential to his miraculous argument that at least one of the states was a non-equilibrium state arrived at by a possibly extremely unlikely fluctuation. In his 1905 analysis of light quanta, Einstein needed to related the entropy of a system with its microscopic constitution in a way that did not rely on a phase space of fixed dimensions, that did not need the presumption of any definite equations of motion and that extended to highly non-equilibrium systems. Einstein argument for Boltzmann's principle met all these demands. In particular, its maddening vagueness is a reflection of the incompleteness of Einstein understanding of quanta. The more precise he made his argument for Boltzmann's principle, the more he risked that the presumptions of his argument might not apply to his target system of light quanta.

1.7 Conclusion

Einstein's miraculous argument for light quanta is a fascinating mix of insecurity and security. It was insecure in that the notion of light quanta directly contradicted the proudest achievement of nineteenth century physics, the wave theory of light. It was secure in that the methods used to infer the existence and properties of light quanta were standard techniques of statistical physics, albeit in an inspired variation. I have urged that by 1905 Einstein had become accomplished in inferring the microscopic constitution of systems from their macroscopic properties and that he was especially familiar with systems consisting of many, independent, spatially localized components. Bolstered with the further empirical evidence of the closing three sections of the paper concerning photoluminescence, the photoelectric effect and the ionization of gases, Einstein could

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[15]For example, free quanta plausibly propagate uniformly in straight lines at the speed of light.

be confident that the light quantum hypothesis was correct. What remained obscure then and later was precisely how the truth of such an extraordinary departure from the wave theory could come about.

I have not advanced any conjectures on the specific historical pathway that Einstein followed to his proposal of the light quantum. However it seems very plausible to me that some role was played by Einstein's familiarity with the macroscopic appearance of systems consisting of many, independent, spatially localized components. It would be interesting to know which signature of discreteness Einstein first found, how early he found it in his conceiving of the light quantum hypothesis and how close it was to the signature actually offered in his 1905 light quantum paper.

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