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Four Calculations, 1904–1905

Fluctuation, Wien entropy, the photoelectric line,
and the mean square displacement

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Abstract. This paper computes four results Einstein published in 1904 and 1905, and it does not repeat the essay on his disagreement with Planck. That disagreement is the site paper *Einstein's Reading of Planck*. The History tab places the same papers in their years. Here each symbol is assigned and each step is the step in the cited primary source. The fluctuation formula is from the 1904 molecular theory [3]. The entropy match and the photoelectric line are §§6–8 of the March 1905 paper [5], using Wien's law [4] and Lenard's fact [6] as inputs, not as a story about inspiration. The diffusion law is the May 1905 paper [8]. Perrin's count [10] is the later measurement, listed as such.

1. What is not repeated

The 1901 capillarity paper and the 1902 electrochemistry paper [1, 2] establish only that Planck is absent. They are not recalculated. The 1906 claim that a resonator energy is an integer multiple of $h\nu$, Planck's letters, and the 1949 gap are not this paper. Shields, *Einstein's Reading of Planck*, already carries them. Nothing below is a second statement of that reading.

2. The 1904 fluctuation

In the notation of a later textbook, a system in weak contact with a bath at temperature T has a weight proportional to $e^{-E/kT}$. With $\beta = 1/(kT)$ and $Z = \sum e^{-\beta E}$, the mean energy and its variance are derivatives of $\log Z$:

$$\langle E\rangle = -\partial(\log Z, \beta), \quad \langle (E - \langle E\rangle)^2\rangle = \partial(\langle E\rangle, \beta)\cdot(-1).$$

Changing the derivative from β to T gives the relation Einstein uses [3],

$$\langle (\Delta E)^2\rangle = kT^2 \frac{d\langle E\rangle}{dT}.$$

Symbols: E is the energy of the system, not a spectral density. k is Boltzmann's constant, which he writes as R/N. T is the absolute temperature of the bath. The 1904 paper applies this identity to black radiation and finds a characteristic length of the order of a wavelength. That application is stated there. It is not a derivation of h, and this paper does not pretend the identity alone is the photoelectric law.

3. From Wien's law to a quantum

Wien's spectral law [4], in the form Einstein uses, makes the entropy of monochromatic radiation of energy E and frequency ν, held in a volume V, change with volume at fixed E by [5]

$$S - S_0 = \frac{E}{\beta\nu}\ln\left(\frac{V}{V_0}\right).$$

Here β is Wien's constant in Einstein's notation, not $1/kT$. S is the entropy of that monochromatic portion. An ideal gas of n independent molecules has, from the 1902 and 1903 statistical papers [11],

$$S - S_0 = kn \ln\left(\frac{V}{V_0}\right).$$

Equating the coefficients of the logarithm,

$$\frac{E}{\beta\nu} = kn, \quad \text{so} \quad E = n \cdot (k\beta\nu).$$

He writes $k = R/N$. The energy of one piece is $(R/N)\beta\nu$. Planck's $h\nu$ is this piece once the constants are identified [5, 12]. The identification is valid where Wien's law holds, which Einstein says in the paper. It is not a derivation of Planck's full formula. That limit is the content of [5], §6. The site paper on the reading of Planck discusses what he refused. This section only equates the two entropies.

4. The photoelectric line

Lenard [6] measured that the speed of the leaving electrons does not rise with intensity, and that a threshold frequency exists. Einstein's §8 [5] does not remeasure this. It assigns the quantum of the previous section to one electron. Of $(R/N)\beta\nu$, a part P is spent leaving the metal. The remainder is kinetic energy. If Π is the positive stopping potential that just prevents escape, and e the charge of the electron,

$$\Pi e = \frac{R}{N}\beta\nu - P. \quad [5]$$

Later notation, not his page: P is the work function φ, and $(R/N)\beta$ is h, so

$$e\Pi = h\nu - \varphi, \quad \text{or} \quad \frac{1}{2}mv_{\max}^2 = h\nu - \varphi.$$

m and $v_{\max}$ are the mass and the greatest speed of the freed electron. Intensity does not appear. It would count how many quanta arrive. The slope of Π against ν is h/e. Millikan [7] measured that slope and recovered h. His paper is the measurement. It is not an endorsement of the light quantum, and he says so. The Nobel citation [13] names this law. It is cited here as a citation, not as a completion of the theory.

The same section of [5] notes Stokes's rule: a quantum $h\nu$ cannot pay for a fluorescent quantum of higher frequency. That is an inequality, $\nu_{\text{out}} \le \nu_{\text{in}}$, not a second mechanism.

5. The mean square displacement

The dissertation [9] relates viscosity and diffusion for spheres in a solvent. It is not used as a quantum paper. The May 1905 paper [8] treats a sphere of radius a in a liquid of viscosity η. Stokes's drag coefficient is $6\pi\eta a$. The osmotic force on a dilute suspension balances that drag and yields the diffusion coefficient

$$D = \frac{RT}{N \cdot 6\pi\eta a} = \frac{kT}{6\pi\eta a}.$$

D is a length squared per time. Along one axis the mean square displacement in a time t is $2Dt$ [8],

$$\langle x^2 \rangle = \frac{RT}{N} \cdot \frac{1}{3\pi\eta a} \cdot t.$$

Every quantity except N is measurable on the suspension. The paper therefore predicts N. Perrin [10] is the count that matched it. His paper is 1909. It is not an assumption of 1905.

6. References

Primary sources for the four calculations, in the order used above. Secondary commentary is not required for the algebra and is not listed.

1. A. Einstein, “Folgerungen aus den Capillaritätserscheinungen,” *Annalen der Physik* 4, 513–523 (1901). Cited only to mark that Planck is absent.
2. A. Einstein, “Über die thermodynamische Theorie der Potentialdifferenz zwischen Metallen und vollständig dissociierten Lösungen ihrer Salze,” *Annalen der Physik* 8, 798–814 (1902). Same purpose.
3. A. Einstein, “Zur allgemeinen molekularen Theorie der Wärme,” *Annalen der Physik* 14, 354–362 (1904). The fluctuation identity.
4. W. Wien, “Über die Energievertheilung im Emissionsspectrum eines schwarzen Körpers,” *Annalen der Physik* 58, 662–669 (1896). The law used as input.
5. A. Einstein, “Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt,” *Annalen der Physik* 17, 132–148 (1905). Entropy match, §6; photoelectric line, §8.
6. P. Lenard, “Über die lichtelektrische Wirkung,” *Annalen der Physik* 8, 149–198 (1902). The measured independence of speed and intensity.
7. R. A. Millikan, “A direct photoelectric determination of Planck’s h,” *Physical Review* 7, 355–388 (1916).
8. A. Einstein, “Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen,” *Annalen der Physik* 17, 549–560 (1905).
9. A. Einstein, “Eine neue Bestimmung der Moleküldimensionen,” dissertation, Bern, 30 April 1905; *Annalen der Physik* 19, 289–306 (1906).
10. J. Perrin, “Mouvement brownien et réalité moléculaire,” *Annales de chimie et de physique* 18, 5–114 (1909).
11. A. Einstein, “Kinetische Theorie des Wärmegleichgewichtes und des zweiten Hauptsatzes der Thermodynamik,” *Annalen der Physik* 9, 417–433 (1902); “Eine Theorie der Grundlagen der Thermodynamik,” *Annalen der Physik* 11, 170–187 (1903). The statistical entropy used for the gas.
12. M. Planck, “Über das Gesetz der Energieverteilung im Normalspectrum,” *Annalen der Physik* 4, 553–563 (1901). Source of the constant later written h, not of the photoelectric derivation.
13. Nobel Prize in Physics 1921, awarded 1922. Citation for the photoelectric law.
14. A. Einstein to C. Habicht, May 1905. *Collected Papers of Albert Einstein*. Ranks the radiation paper among the year’s work. Not a derivation.