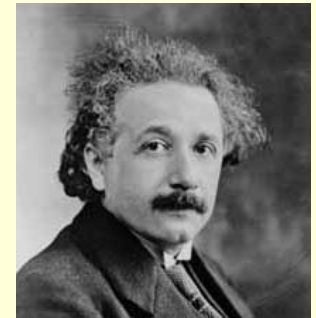
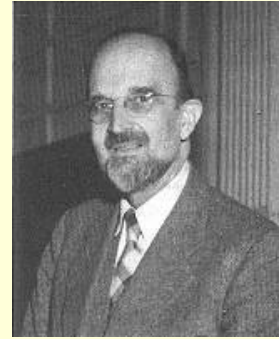


**WALTHER NERNST,**

**ALBERT EINSTEIN,**

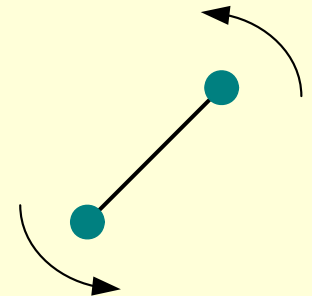
**OTTO STERN, ADRIAAN FOKKER,**



**AND**

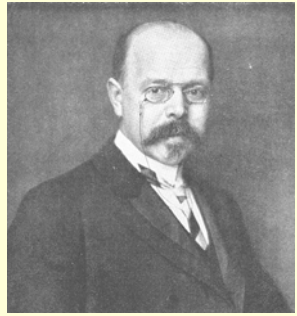
**THE ROTATIONAL SPECIFIC HEAT OF HYDROGEN**

Clayton Gearhart  
St. John's University  
(Minnesota)

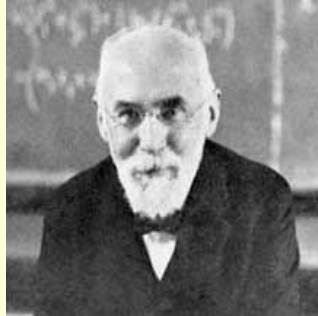


Max-Planck-Institut für Wissenschaftsgeschichte  
Berlin  
July 2007

# ROTATIONAL SPECIFIC HEAT OF HYDROGEN: WIDELY INVESTIGATED IN THE OLD QUANTUM THEORY



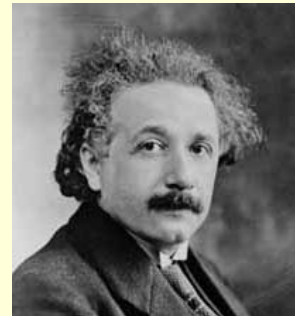
Nernst



Lorentz



Eucken



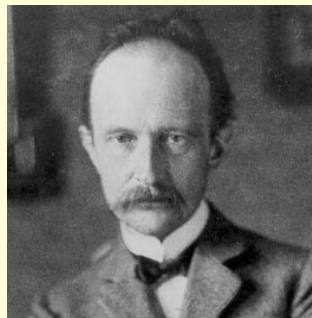
Einstein



Ehrenfest



Bohr



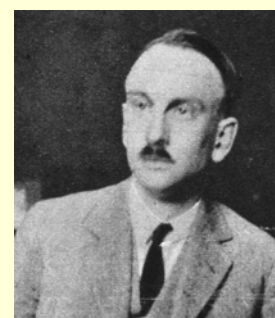
Planck



Reiche



Kemble



Tolman



Schrödinger

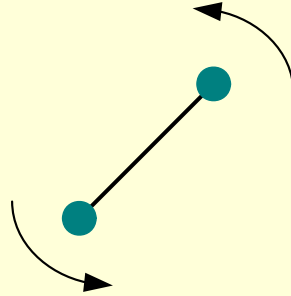


Van Vleck

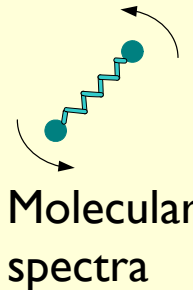
Some of the more prominent physicists and physical chemists who worked on the specific heat of hydrogen through the mid-1920s.

See “The Rotational Specific Heat of Molecular Hydrogen in the Old Quantum Theory”  
[http://faculty.csbsju.edu/cgearhart/pubs/sel\\_pubs.htm](http://faculty.csbsju.edu/cgearhart/pubs/sel_pubs.htm) (slide show)

# RIGID ROTATOR (ROTATING DUMBBELL)

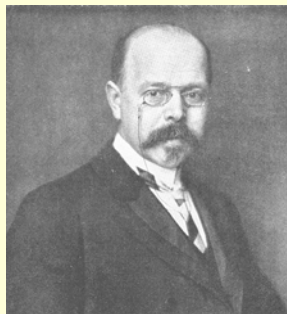


- The **rigid rotator** was among the earliest problems taken up in the **old (pre-1925) quantum theory**.
- **Applications:** Molecular spectra, and rotational contribution to the specific heat of molecular hydrogen
- **The problem should have been simple**
  - relatively uncomplicated theory
  - only one adjustable parameter (moment of inertia)
- Nevertheless, **no satisfactory theoretical description of the specific heat of hydrogen emerged** in the old quantum theory



**OUR STORY BEGINS WITH**

# NERNST'S HEAT THEOREM



Walther Nernst

1864 — 1941

- physical chemist
- studied with Boltzmann
- 1889: lecturer, then professor at Göttingen
- 1905: professor at Berlin

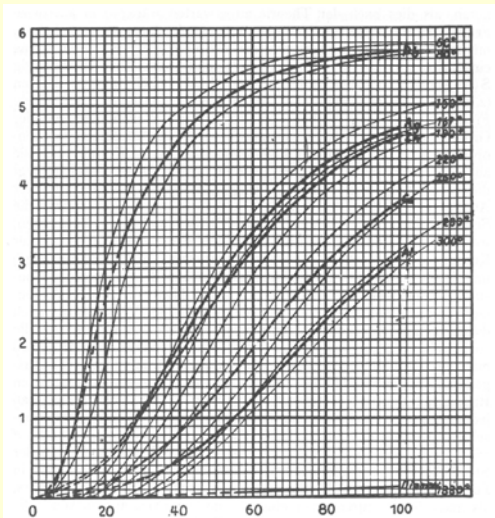
Nernst formulated his heat theorem (Third Law) in 1906, shortly after appointment as professor in Berlin.

# NERNST'S HEAT THEOREM AND QUANTUM THEORY

- Initially, had nothing to do with quantum theory.
- Understand the equilibrium point of chemical reactions.
- **Nernst's theorem had implications for specific heats at low temperatures.**
- 1906–1910: Nernst and his students undertook extensive measurements of specific heats of solids at low (down to liquid hydrogen) temperatures.

**“... one gets the impression that the specific heats are converging to zero as required by Einstein's theory.”** (Nernst 1910)

- Einstein in 1907: If one treated a solid as a collection of quantized harmonic oscillators, the specific heat should go to zero as  $T \rightarrow 0$ .
- As a result, Nernst became an enthusiastic promoter of quantum ideas.



Nernst's data  
(February 1911)

**... Nernst, who rescued all  
the results pertaining to this  
question from their  
theoretical limbo...**

Einstein (1911)  
(Solvay Conference)

# THE SPECIFIC HEAT OF MOLECULAR HYDROGEN

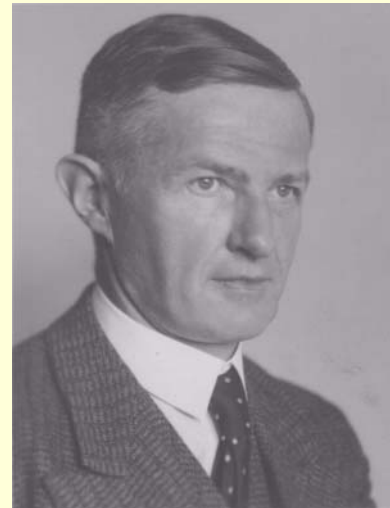
- Initially, Nernst's Heat Theorem applied only to solids and liquids
- Early in 1911, Nernst speculated that the rotational (and for diatomic gases, vibrational) degrees of freedom **for gases** might show quantum behavior.
- Because of its low mass and low liquification temperature,

... **The determination of the specific heat of hydrogen at low temperatures would therefore be especially interesting. (Nernst 1911)**

Arnold Eucken was one of Nernst's assistants, and had been closely involved in the measurements of the specific heats of solids.

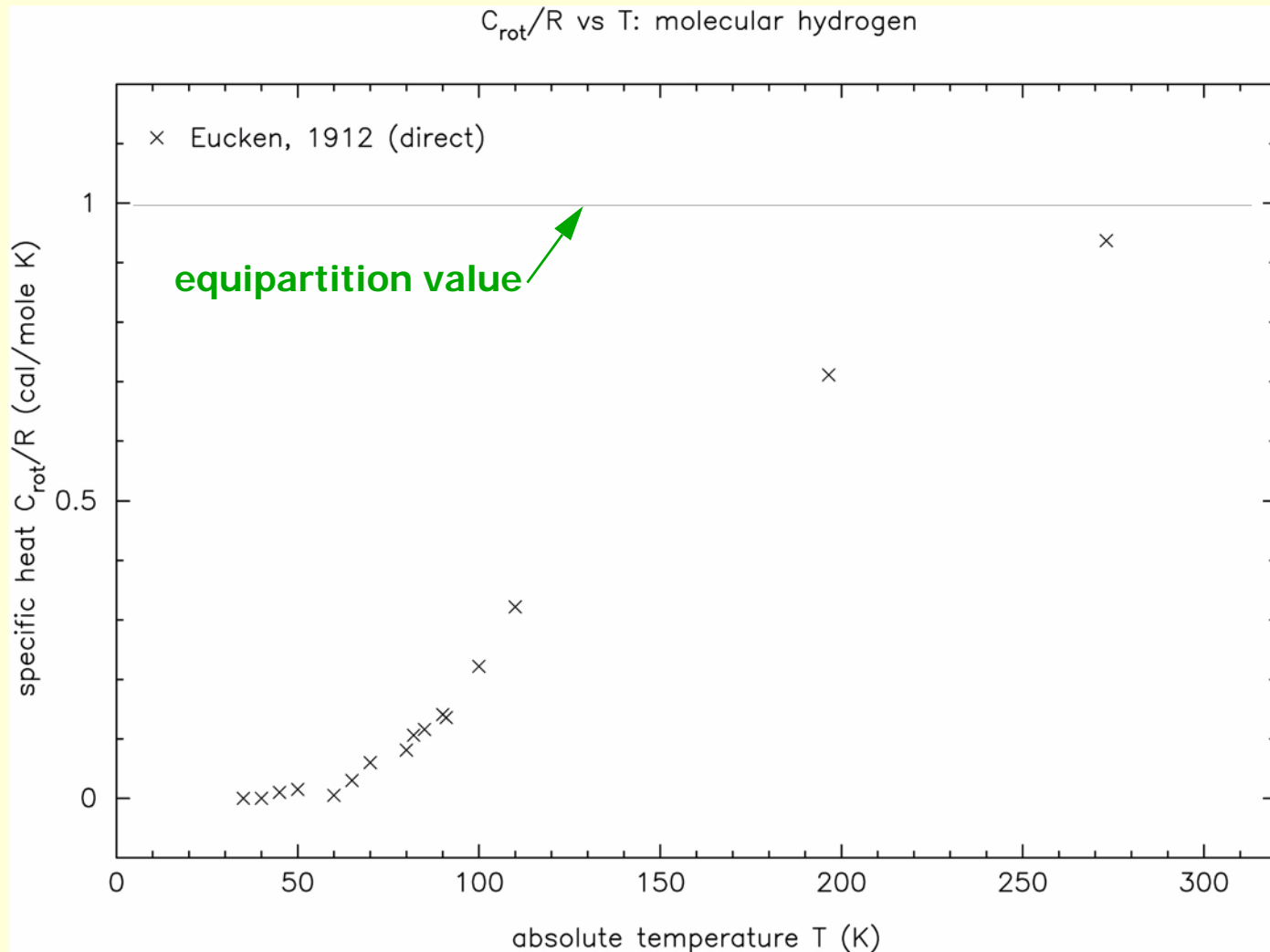
In 1912, he packed about 0.2 moles of  $H_2$  into a  $39\text{ cm}^3$  thin-walled steel chamber (pressure about 100 atm!), measured the specific heat down to about 30K.

Both the experiment and the data reduction were difficult. Eucken found ...



Arnold Eucken

# EUCKEN'S DATA



Eucken attempted to fit these data to Einstein's 1907 result for the specific heat of solids.

# AND NOW, THE THEORY

## QUANTUM THEORY OF THE RIGID ROTATOR APPLIED TO THE SPECIFIC HEAT OF HYDROGEN

### STAGES

1. The unquantized rotator: Nernst, Einstein, Otto Stern, and Adriaan Fokker, 1911–1914

### THEME

**... the thermal energy of every structure depends on the temperature in the same way as that of the resonators in Planck's theory ...**

Einstein, "Max Planck as Scientist," 1913

2. Quantized rotators with one degree of freedom: Lorentz, Paul Ehrenfest, Erik Holm, others; 1913–1916 or so
3. Quantized rotators with two degrees of freedom: Max Planck, Fritz Reiche, Edwin C. Kemble, Niels Bohr, others; 1915–1925. Increasingly close connection to molecular spectra through mid-1920s
4. Modern quantum mechanics: John Van Vleck, Friedrich Hund, David Dennison, others; 1926 on



# NERNST, FEBRUARY 1911

“Towards a theory of specific heats and on the application of the doctrine of energy quanta to physical chemical questions in general”

Zeitschrift für Electrochemie, 1911

... I will derive Einstein's formula not deductively from the general principles of statistical mechanics, but on the contrary **through the direct calculation of a special simple case**, through which I hope to formulate the considerations **transparently and visually**.

Nernst 1911

## EINSTEIN ON NERNST:

Nernst's standard work, “Theoretical Chemistry,” offers, not only to the student but also to the scholar, an abundance of stimulating ideas; it is theoretically elementary, but clever, vivid, and full of intimations of manifold interrelations. It truly reflects his intellectual character.

Einstein (1942)

# NERNST AND SPECIFIC HEATS: FEBRUARY 1911

“Towards a theory of specific heats and on the application of the doctrine of energy quanta to physical chemical questions in general”

Zeitschrift für Electrochemie, 1911

Nernst began by pointing out problems with equipartition in monatomic and diatomic gases:

- monatomic gases: experimentally, no rotational degrees of freedom. **The theory furnishes not even a clue ...**
- diatomic gases: value  $5/2 R$  is ok for most gases, but halogens have considerably higher values, and the specific heats of all diatomic gases increase at higher temperatures.

**The theory can account for a new degree of freedom, as in the oscillation of an atom around its equilibrium position, but the gradual emergence of a new degree of freedom is (without new arbitrary assumptions) entirely senseless.**

# NERNST AND SPECIFIC HEATS: FEBRUARY 1911

Nernst first considered a mass point oscillating in a 3D solid, and attempted to treat its three degrees of freedom:

we can so visualize the motion of a point, that we project its path onto three mutually perpendicular planes, whereby we obtain three “oscillation circles” [“Schwingungskreise”].

Since we at first disregard the quantum theory and make the assumption, that the kinetic energy of the Schwingungskreise projected on a plane ... sits in equilibrium with the kinetic energy of the gas molecules projected on the same plane, we arrive at the second consequence, that in both cases the same distribution law obtains.

That distribution turns out to be the Maxwell-Boltzmann velocity (not speed) distribution. Nernst applied the Maxwell-Boltzmann distribution **to a solid**. He **quantized** the Maxwell-Boltzmann distribution for solids, and derived Einstein's specific heat formula.

Finally, he assumed that a gas molecule which crashes (anprallt) onto a rotating atom ... is able to take on or withdraw only the energy quantum

$$\epsilon = h\nu$$

# NERNST AND SPECIFIC HEATS: FEBRUARY 1911

## THE UNQUANTIZED QUANTUM ROTATOR

### Rotational motion:

If we make the certainly obvious generalization of the quantum hypothesis, that **energy always will be absorbed only in fixed quanta not only for an oscillation about an equilibrium position, but also for an arbitrary rotation of masses**, then we arrive at the wider conclusion that certain contradictions of the old theory may perhaps be clarified.

### Summary of Nernst's theory

- A diatomic gas molecule exchanges rotational energy with a Planck resonator in fixed (harmonic oscillator) quanta;
- Assumes for simplicity that rotational velocities of all gas molecules are the same (even though one expects a Maxwell-Boltzmann distribution);
- Equipartition: Assume rotational velocity is proportional to the square root of the temperature (that is,  $KE \sim kT$ ). Einstein pointed out the inconsistency later that year.
- **Neither the rotational velocity nor the rotational energy is quantized!**

# NERNST AND SPECIFIC HEATS: FEBRUARY 1911

Through this chain of reasoning, Nernst writes the following results:

Nernst's (and Einstein's) result for the average energy of a collection of quantized Planck oscillators

$$W = 3R \frac{\beta\nu}{e^{\frac{\beta\nu}{T}} - 1} \quad \text{derivative} \Rightarrow \text{Einstein's result for the specific heat}$$

$$\frac{dW}{dT} = 3R \frac{e^{\frac{\beta\nu}{T}} \left( \frac{\beta\nu}{T} \right)^2}{\left( e^{\frac{\beta\nu}{T}} - 1 \right)^2}$$

↓

$$\beta\nu = a\sqrt{T} \quad \text{equipartition result, substituted into } W$$

↓

derivative now leads to

$$\frac{R}{4} \left[ \frac{a}{\sqrt{T} \left( e^{\frac{a}{\sqrt{T}}} - 1 \right)} + \left( \frac{a}{\sqrt{T} \left( e^{\frac{a}{\sqrt{T}}} - 1 \right)} \right)^2 e^{\frac{a}{\sqrt{T}}} \right]$$

Nernst's result for the specific heat per degree of freedom of a diatomic molecule.

Nernst showed that this expression leads to the expected result (rotational contribution to specific heat =  $R$ ) for oxygen molecule at room  $T$ .

# FIRST SOLVAY CONFERENCE (NOV 1911): EINSTEIN

At the first Solvay Conference in November 1911, Nernst talked about his specific heat measurements for solids, but said comparatively little about gases.

**HOWEVER ...**

Einstein devoted a short section to the rigid rotator in his talk:

- I tried to solve this problem, but did not succeed because of mathematical difficulties.
- Then, adopted a corrected version of Nernst's model:

**Nernst assumed the relation  $\beta\nu = a\sqrt{T}$ . But this relation could only be satisfied if the specific heat were independent of the temperature.**

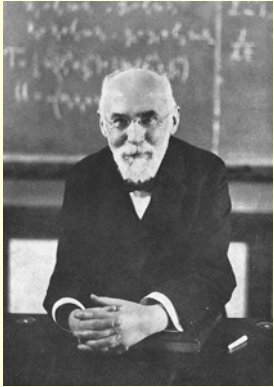
$$\begin{array}{ccc} \text{kinetic energy} & \longrightarrow & \frac{1}{2} J (2\pi\nu)^2 = \frac{h\nu}{e^{h\nu/kT} - 1} \longleftarrow \\ \text{of rotator} & & \text{average energy of} \\ & & \text{Planck oscillator} \end{array}$$

**... all that remains is to eliminate  $\nu$**

The rotator is **not** quantized. Does it nevertheless absorb/give off quanta  $h\nu$ , as Nernst had supposed? Einstein said nothing about physical interpretation.

**THERE WAS ONE MORE CONTRIBUTION TO THE DISCUSSION:**

# FIRST SOLVAY CONFERENCE: LORENTZ



## QUANTIZING THE RIGID ROTATOR

Lorentz:

Quantize the rotator energy directly  
(comment following Einstein's report):

$$\frac{1}{2} J (2\pi\nu)^2 = n h \nu, \quad n = 0, 1, 2, \dots$$

whence

$$\nu = n \frac{h}{2\pi^2 J}$$

$J$  = moment of  
inertia

$\nu$  = frequency of  
rotation

$$\frac{1}{2} J (2\pi\nu)^2 = n^2 \frac{h^2}{2\pi^2 J}$$

**But then, this remark is of no great significance. When applying the hypothesis of energy elements, one can confine oneself to systems for which a definite frequency determined by the nature of the process is given in advance.**

# FIRST SOLVAY CONFERENCE: DISCUSSION

It appears to me that the introduction of the energy elements ... is only admissible, if the system has a definite frequency...

It therefore appears arbitrary [willkürlich] to apply the quantum hypothesis to the rotation of molecules.

Paul Langevin

The assumption that a diatomic gas molecule, which rotates with frequency  $\nu$ , can take on only quanta of size  $h\nu$ , is wholly inadmissible. ...

Frederick Lindemann



# EINSTEIN, OTTO STERN, AND ZERO-POINT ENERGY: 1913

## “Some arguments for the Assumption of Molecular Agitation at Absolute Zero”

(January 1913)



Otto Stern

$$\frac{1}{2} J (2\pi\nu)^2 = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} \leftarrow \text{zero-point energy}$$

“Planck’s first theory:”

- Quantized energy levels
- No zero-point energy

“Planck’s second theory:” (1911)

- Continuous energies
  - Energy quanta emitted when resonator is on the boundary of a **finite** phase-space cell
  - Quantized energy replaced by the **average** energy within a **finite** phase-space cell.
- ⇒ leads to “zero-point energy” of sorts

**Einstein and Stern investigated zero-point energies, but did NOT adopt Planck’s second theory.**

Stern did his Ph.D. with Otto Sakur in Breslau in 1912. Sakur had worked with Nernst, and published a series of papers (“Sakur-Tetrode equation”) on quantizing the monatomic ideal gas.

# EINSTEIN AND STERN, 1913

## THE UNQUANTIZED QUANTUM ROTATOR

$$E = \frac{1}{2} J (2\pi\nu)^2 = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2}$$

zero-point energy

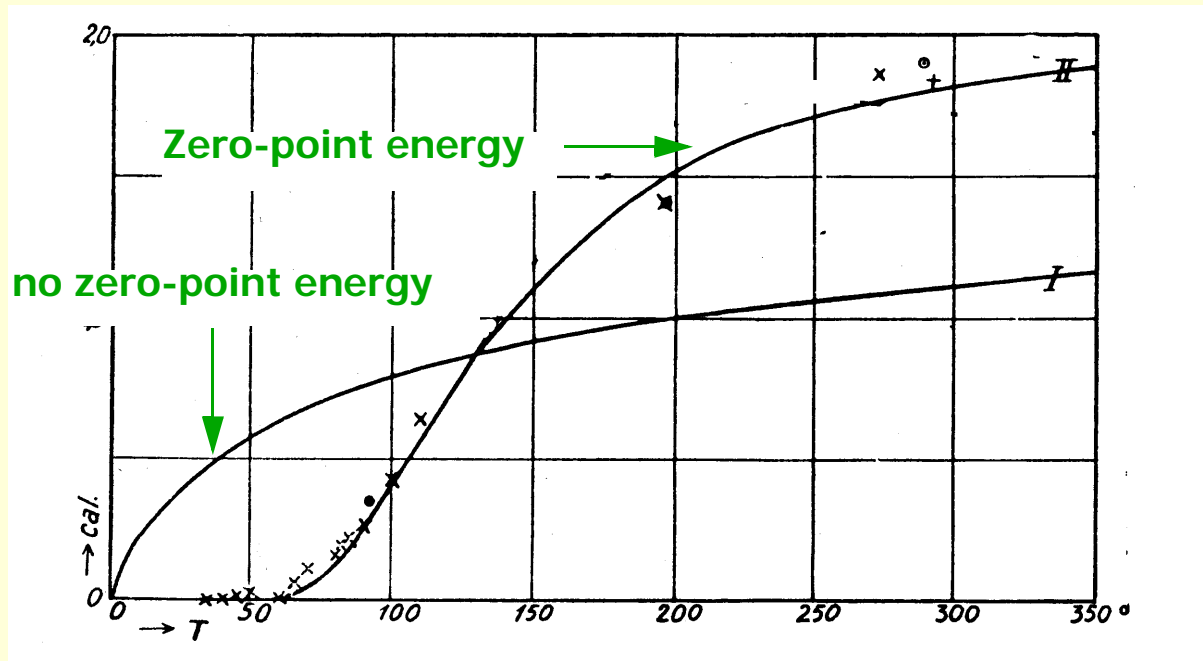
$dE/dT$  gives the specific heat; one solves a transcendental equation to find  $\nu(T)$

**Since the rotator frequency is a function of temperature, the zero-point energy contributes to the specific heat.**

**... [the specific heats] are equivalent for structures with unchanging  $\nu$ , whereas the theory of those structures whose  $\nu$  has different values for different states is substantially affected by the assumption of a zero-point energy.**

Note that rotator frequency  $\nu(T)$  and energy are *continuous* (and fairly weak) functions of temperature! The rotators are *not* quantized, but do rotate at the frequency of the oscillator.

# EINSTEIN AND STERN: RESULTS



Einstein and Stern remarked on the “**splendid agreement**” of their zero-point calculation with Eucken’s results.

Ironically, the agreement was at least as good as anyone else would achieve over the next 15 years!

**What was their physical picture?** Was it the same as Nernst’s—rotators exchanging harmonic oscillator quanta with Planck resonators? To answer this question, we must consider ...

## SECOND PART OF EINSTEIN-STERN PAPER

# FLUCTUATIONS AND ZERO-POINT ENERGIES

The study of fluctuations (including Brownian motion) was a continuing theme in Einstein's work, starting in 1904, and continuing through the famous *A* and *B* coefficients paper in 1916. For Einstein, these fluctuations were a probe into a theory that did not yet exist!

**...the fluctuation properties of radiation ... offer few formal clues on which to build a theory.**

Einstein 1909

**1909:** Wave-particle duality



**1910:** (with Ludwig Hopf):  
Planck's radiation law incompatible  
with Maxwell's laws



**1913:** Einstein and Stern extended 1910  
derivation to include zero-point energy



**1916:** Fluctuations were  
central in the famous *A* and *B*  
coefficients paper.

# 1909: FLUCTUATIONS AND THE WAVE-PARTICLE DUALITY

**MOMENTUM FLUCTUATIONS:** A moving mirror in equilibrium with a radiation field

- experiences a damping force  $P$  akin to friction
- also experiences irregular pressure (momentum) fluctuations  $\Delta$  exerted by radiation.
- Equilibrium requires that the mean square velocities at  $t$  and a short time  $\tau$  later be equal. This condition leads to

$$\frac{\overline{\Delta^2}}{\tau} = \frac{3kT}{c} \left( \rho - \frac{\nu}{3} \frac{d\rho}{d\nu} \right) f d\nu$$

$\rho =$  radiation density  
 $f =$  area of mirror

momentum fluctuations  $\nearrow$   $\nwarrow$  damping force  $P$

Substitution of Planck's radiation law for  $\rho$  to leads to

$$\rho = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

$$\frac{\overline{\Delta^2}}{\tau} = \frac{1}{c} \left( h\nu\rho + \frac{c^3}{8\pi} \frac{\rho^2}{\nu^2} \right) f d\nu$$

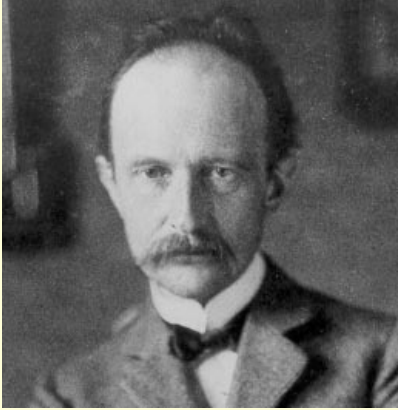
particle term (light quanta)  $\nearrow$

$\nwarrow$  wave term (Maxwell's laws)

Einstein (1909) spoke of

**... a theory of light that can be understood as a kind of fusion of the wave and emission theories of light.**

# 1909: THE REACTION



... the interaction between free electrical energy in a vacuum and the motion of material atoms ... is in essence based on the emission and absorption of light. ... **Well, the emission and absorption is just the dark point about which we know very little. ...**

... one should try first to shift all of the difficulties of quantum theory to the realm of *interaction* between matter and radiant energy...

Max Planck, 1909

# 1910: FLUCTUATIONS AND THE RAYLEIGH-JEANS LAW

In 1910, Einstein and his assistant Ludwig Hopf showed just how fundamentally Planck's radiation law challenged earlier physics:

- Gas of Planck resonators (oscillating dipoles) in equilibrium with radiation
- Derivation assumes **equipartition only for translational motion** of resonators.
- Calculate the momentum fluctuations **independently**, using Maxwell's laws
- Treat the radiation density as an **unknown**

The 1909 result  $\frac{\overline{\Delta^2}}{\tau} = \frac{3kT}{c} \left( \rho - \frac{\nu}{3} \frac{d\rho}{d\nu} \right) f d\nu$  (where  $f$  is now the dipole moment) becomes (after canceling some constants)

momentum fluctuation term, calculated from Maxwell's laws

$$\longrightarrow \frac{c^2}{8\pi} \frac{\rho^2}{\nu^2} = \frac{3kT}{c} \left( \rho - \frac{\nu}{3} \frac{d\rho}{d\nu} \right) \longleftarrow \text{damping force } P$$

The momentum fluctuation term on the left looks like the wave-like fluctuation Einstein had found in 1909. Not surprisingly, the solution to this differential equation is the impossible Rayleigh-Jeans law.

$$\rho = \frac{8\pi\nu^2}{c^3} kT$$

“ultraviolet catastrophe”

Paul Ehrenfest

# 1913: FLUCTUATIONS AND ZERO-POINT ENERGIES

Einstein and Stern repeated the Einstein-Hopf calculation, but this time assumed the resonator had a zero point energy  $h\nu$  (NOT  $h\nu/2$ ).

- Both energy density and average resonator energy were taken as unknowns.

**Result:** 
$$\frac{1}{c} \left( h\nu\rho + \frac{c^2}{8\pi} \frac{\rho^2}{\nu^2} \right) = \frac{3kT}{c} \left( \rho - \frac{\nu}{3} \frac{d\rho}{d\nu} \right) \leftarrow \text{damping force}$$

momentum fluctuations  
due to zero-point energy

momentum fluctuations due to  
radiation absorption and emission

Solution: Planck's radiation law: 
$$\rho = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

The average resonator energy is  
therefore

$$E = \frac{h\nu}{e^{h\nu/kT} - 1} + h\nu$$

... without recourse to any kind of discontinuities.

**DIFFERENT ZERO-POINT ENERGIES  $\Rightarrow$  SPECIFIC HEAT OF HYDROGEN  
 $\Rightarrow$  ELIMINATE NEED FOR QUANTA**

Is quantum theory entirely a matter of zero-point energies?



# CAVEATS: FLUCTUATIONS AND ZERO-POINT ENERGIES

... the zero-point energy must be set equal to  $h\nu$  in order to arrive at the Planck radiation formula. Future investigations must show whether the discrepancy between this assumption and the assumption underlying the investigation of hydrogen [ $h\nu/2$ ] disappears if the calculation is more rigorous.

... it seems doubtful that other difficulties can be overcome without the assumption of quanta.

Einstein and Stern, January 1913

In spite of what Einstein and Stern called “**splendid agreement**” with Eucken’s data for hydrogen, Einstein soon lost confidence in this calculation, as he announced at the second Solvay Conference (October 1913) and it vanished from sight. By the end of 1913, in a letter to Ehrenfest (V, 481), Einstein pronounced zero-point motion “**dead as a doornail**” (“**maustot ist**”).

Einstein on Eucken’s data, summer 1913, notes of Walter Dällenbach (CPAE 4)

**Kein Teufel weiss warum und nach welchem Gesetz.**  
**(The Lord only knows why and according to what law.)**

# THE LAST ACT: EINSTEIN, ADRIAAN FOKKER, BROWNIAN MOTION, AND THE SPECIFIC HEAT OF HYDROGEN

**1905:** Einstein's first Brownian motion paper:

- derived a diffusion equation to calculate the mean-square displacement of small particles suspended in a viscous fluid due to “**thermal molecular motion.**”

Result:

$$\sqrt{x^2} \sim \sqrt{t}$$

**1906:** Einstein's second Brownian motion paper:

- derived a differential equation for the equilibrium distribution function  $W$  describing any “**arbitrary observable parameter of a physical system.**”
- used this equation to confirm 1905 result, but also to find a similar result for angular displacement.

Result:

(Fokker's notation)

$$W(q)f(q)\tau + \frac{1}{2}\overline{R^2}\frac{dW}{dq} = 0$$

$q$  is the “arbitrary observable parameter”

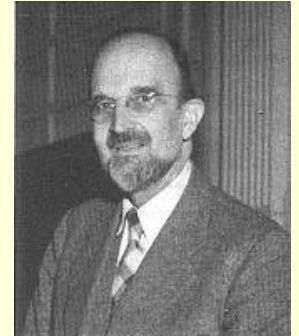
$$f(q) = -dq / dt$$

$\overline{R^2}$  is the mean square average change in  $q$  in time  $\tau$  due to random thermal processes

# THE LAST ACT: EINSTEIN, ADRIAAN FOKKER, BROWNIAN MOTION, AND THE SPECIFIC HEAT OF HYDROGEN

Adriaan Fokker

- 1913: Ph.D. with Lorentz
- 1913: came to Zürich in fall of 1913 to work with Einstein
- made rapid progress, described in letter from Fokker to Lorentz, 4 December 1913
- paper submitted to *Annalen* in late December 1913



**Problem:** Specific heat of Hydrogen

**Approach:** Consider a system of electric dipoles rotating about fixed axes in a Planck radiation field. For the parameter  $q$ , take the angular momentum, and using Einstein's 1906 Brownian motion equation, find equilibrium distribution, average energy, and specific heat.

**What is different from Einstein-Stern?** Calculation allows for a *distribution* of angular velocities; and no reliance whatever on equipartition.

**Difficulty:** Had to find more general form of Einstein's 1906 equation.

**Result:**

# THE LAST ACT: EINSTEIN, ADRIAAN FOKKER, BROWNIAN MOTION, AND THE SPECIFIC HEAT OF HYDROGEN

$$W(q)f(q)\tau - W(q)\bar{R} + \frac{1}{2} \frac{\partial}{\partial q} \left\{ W(q)\overline{R^2} \right\} = 0 \quad \text{“Fokker-Planck equation”}$$

Einstein and Fokker were both surprised that the middle term was needed; but with it,

- derived Planck’s standard result for the relation between radiation density and the average resonator energy, for a collection of resonators in a radiation field

$$u_\nu = \frac{8\pi\nu^2}{c^3} E_{\text{res}}$$

- Showed that a collection of rotators in a Rayleigh-Jeans radiation field obeys a Maxwell-Boltzmann distribution
- **However:** a collection of rotators in a Planck radiation field yields a complicated and unlikely distribution function, and an impossible result (concave down) for the specific heat of hydrogen.

**One can hardly think of a reason, why the same method was successful there, and here cannot be used.**

Fokker 1914

# OTHER OPTIONS: QUANTIZING THE RIGID ROTATOR

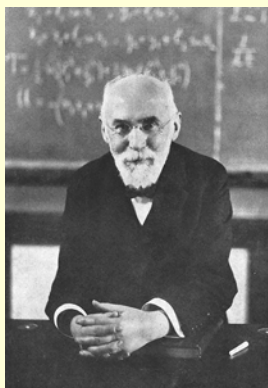


Paul Ehrenfest, 1913

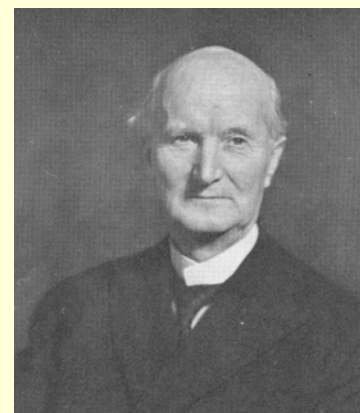
**“Remark concerning the specific heat of diatomic gases”**

Used partition function technique to calculate the specific heat of hydrogen

Einstein had applied the same technique to solids in 1907



H. A. Lorentz, First Solvay Conference, 1911



Niels Bjerrum, 1912

(Danish physical chemist, working in Nernst's laboratory)

**“On the Infrared Absorption Spectra of Gases”**

**... the thermal energy of every structure depends on the temperature in the same way as that of the resonators in Planck's theory ...**

Einstein, “Max Planck as Scientist,” 1913

# THE LAST WORD: ARNOLD EUCKEN IN 1914



After reviewing the Einstein-Stern and Ehrenfest calculations, ...

Finally let us point out a calculation by M. Trautz based on an entirely different standpoint: Let us assume there are at hand two different isomeric modifications of hydrogen, ... a “cold modification” ( $C_v = \frac{3}{2}R$ ) and a “warm modification” ( $C_v = \frac{5}{2}R$ ). Then one can by consideration of the heat of isomerization reproduce equally well the temperature dependence of the molar heat of hydrogen. To be sure one will in general hardly support such an alternative to quantum theory ... **Still, this attempt shows especially clearly how difficult it is, in spite of the availability of the necessary experimental foundation, to arrive at an unambiguous theory.**

Arnold Eucken, 1914  
Appendix to German edition of Solvay I Proceedings

## A FEW REFERENCES

Alexi Assmus, “The molecular tradition in early quantum theory” and “The Americanization of molecular physics,” *Historical Studies in the Physical and Biological Sciences* **22**, 209–231 and **23**, 1–34 (1992)

Diana Kormos Barkan, *Walther Nernst and the Transition to Modern Physical Science* (Cambridge U. Press, Cambridge and New York, 1999)

Martin J. Klein, *Paul Ehrenfest: Vol. I, The Making of a Theoretical Physicist* (North Holland, New York, 1970); and “Einstein and the Wave-Particle Duality,” *Natural Philosopher* **3**, (1964), 3–49.

Peter W. Milonni, *The Quantum Vacuum: An Introduction to Quantum Electrodynamics* (Ch. I) (Academic Press, New York, 1994); and P. W. Milonni and M. -L. Shih, “Zero-point energy in early quantum theory,” *American Journal of Physics* **59** (1991), 684–698

Luis Navarro and Enric Pérez, “Paul Ehrenfest: The Genesis of the Adiabatic Hypothesis, 1911–1914,” *Archive for History of Exact Sciences* **60** (2006), 209–267.

Allan A. Needell, Ph.D. dissertation, Yale University (1980).

Jos Uffink, “Insuperable difficulties: Einstein’s statistical road to molecular physics,” *Studies in History and Philosophy of Modern Physics* **37** (2006), 36–70.