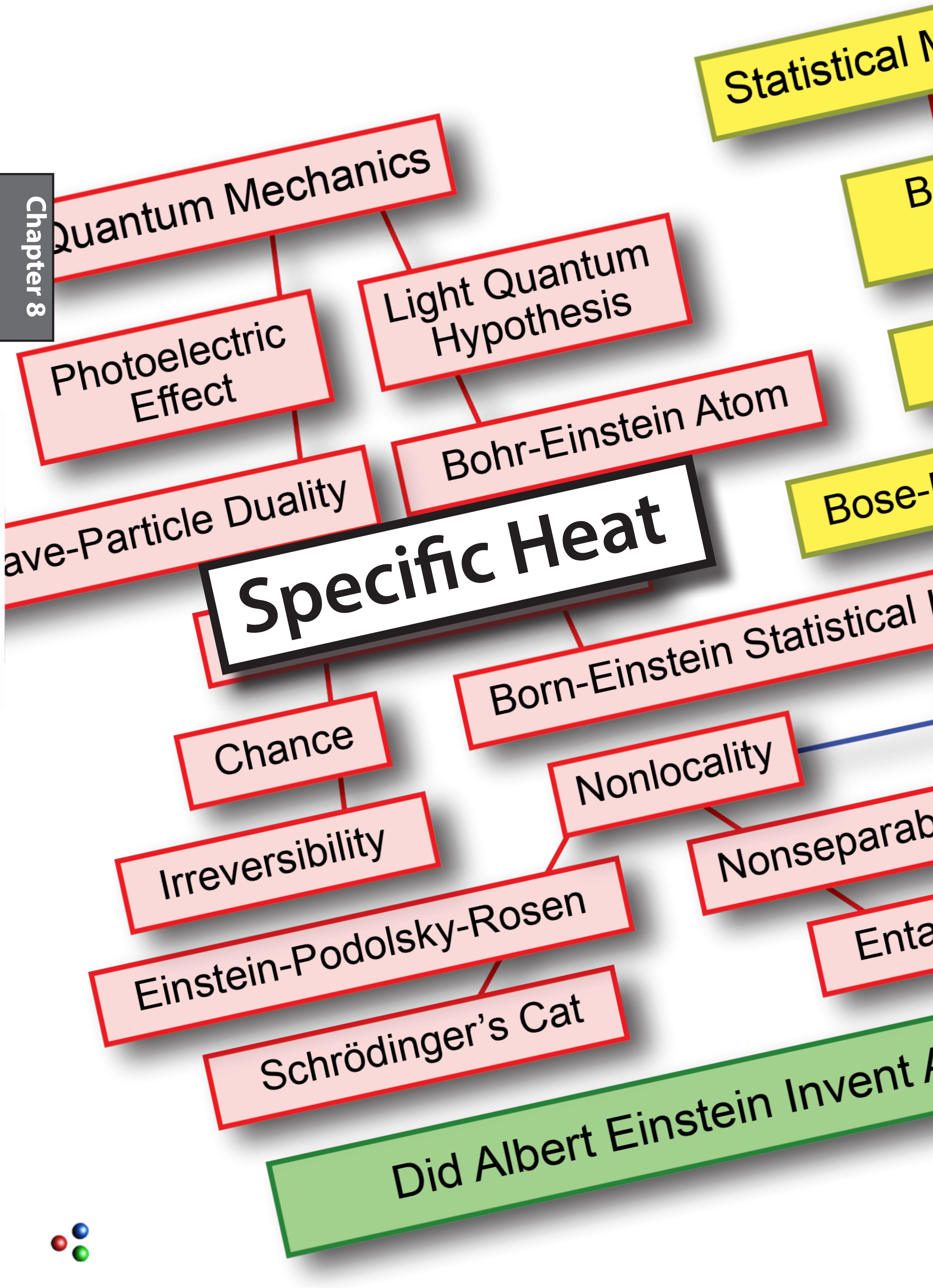
Chapter 8


Statistical
Quantum Mechanics
Light Quantum Hypothesis
Photoelectric Effect
Bohr-Einstein Atom
Particle Duality
Specific Heat
Born-Einstein Statistical
Chance
Nonlocality
Irreversibility
Einstein-Podolsky-Rosen
Schrödinger's Cat
Did Albert Einstein Invent

Specific Heat

A few months after the three famous papers of his miracle year, Einstein published in September 1905 a three-page paper showing that energy and matter are interconvertible according to the famous equation $E = mc^2$. This result greatly strengthened his belief in the light quantum hypothesis of March. He now saw that radioactive decay involves the liberation of a vast amount of radiation which is a consequence of the conversion of mass into energy. This was forty years before the first atomic bomb.

In 1906 and early 1907, Einstein published two more papers on the Planck radiation law and the deeper physical connections that must exist between matter and radiation. The first was on the emission and absorption of radiation by matter, the second on the specific heat of different materials.

In the first paper, Einstein was puzzled how Planck had arrived at his law for the distribution of energy in blackbody radiation, especially the exponential factor in the denominator and the added *-1*. He concluded (ironically?) that Planck had effectively, without understanding it, "introduced into physics a new hypothetical element: the hypothesis of light quanta." He wrote

> the energy of an elementary resonator can only assume values that are integral multiples of (R/N)β*v* : by emission and absorption, the energy of a resonator changes by jumps of integral multiples of (R/N)β*v*. (In modern notation, *hv*.)

Einstein thus introduced "quantum jumps" inside atoms six years before Niels Bohr's atomic model with Bohr's proposal for "stationary states" or energy levels. Forty-five years later, Erwin Schrödinger denied quantum jumps in two articles,[1] John Bell questioned them again in 1986,[2] and decoherence theorists deny the "collapse of the wave function" to this day.

Einstein's paper of 1907 was an extraordinary investigation into the *specific heat* of solid materials. In this paper, Einstein again

1 "Are There Quantum Jumps?," *British Journal for the Philosophy of Science* 3.10 (1952):

2 "Are There Quantum Jumps?" in *Schrödinger, Centenary of a Polymath* ed. C. Kilmister, Cambridge University Press (1987)

took the implications of Planck's quantum theory more seriously than had Planck himself. Matter must have internal quantum states.

Internal quantum states at energies higher than the ground state will not be populated unless there is enough energy available to cause a jump from the ground state to one or more of the "excited" states. The populations of higher states are proportional to the "Boltzmann factor" $e^{-E/kT}$.

There are many kinds of states in atoms, molecules, and in the so-called "solid state," atoms arranged in lattice structures like crystals and metals. The quantum states correspond to classical "degrees of freedom." A molecule can rotate in two orthogonal directions. It can vibrate in one dimension, the distance between the atoms. Atoms and molecules have excited electronic states. In general, rotational states have the lowest energy separations, vibrational states next, and electronic states the highest energies above the ground state. And bulk matter vibrates like a violin string or a sound wave (phonons).

Specific heat is the amount of energy that must be added to raise the temperature of material one degree. It is closely related to the entropy, which has the same dimensions - ergs/degree. It depends on the quantum internal structure of the material, as first understood by Einstein, who is sometimes recognized as the first solid-state physicist.

As the temperature increases, the number of degrees of freedom, and thus the number of states (whose logarithm is the entropy), may all increase suddenly, in so-called phase changes (the number of available cells in phase space changes).

Conversely, as temperature falls, some degrees of freedom are said to be "frozen out," unavailable to absorb energy. The specific heat needed to move one degree is reduced. And the entropy of the system approaches zero as the temperature goes to absolute zero.

Some diatomic molecular gases were known to have anomalously low specific heats. It had been one of the strong arguments against the kinetic-molecular theory of heat. In a monatomic gas, each atom has three degrees of freedom, corresponding to the three independent dimensions of translational motions, *x, y,* and *z.*

A diatomic molecule should have six degrees of freedom, three for the motion of the center of mass, two for rotations, and one for vibrations along the intramolecular axis.

While some diatomic materials appear to have the full specific heat expected if they can move, rotate, and vibrate, it was Einstein who explained why many molecules can not vibrate at ordinary temperatures. The vibrational states are quantized and need a certain minimum of energy before they can be excited.

Einstein's research into specific heats suggested that internal molecular quantum states could account for emission and absorption lines and the continuous bands seen in spectroscopy.

Einstein speculated that the vibrational states for some molecules were too far above the ground state to be populated, thus not absorbing their share of energy when heat is added). Most diatomic molecules were known to have a specific heat *c* of 5.94, but Einstein said that according to Planck's theory of radiation, their specific heat would vary with temperature. He found

$c = 5.94\ \beta\nu\ / e^{\beta\nu/T} - 1.$

Einstein plotted a graph to show his increase in specific heat with temperature, along with a few experimental measurements.[3]

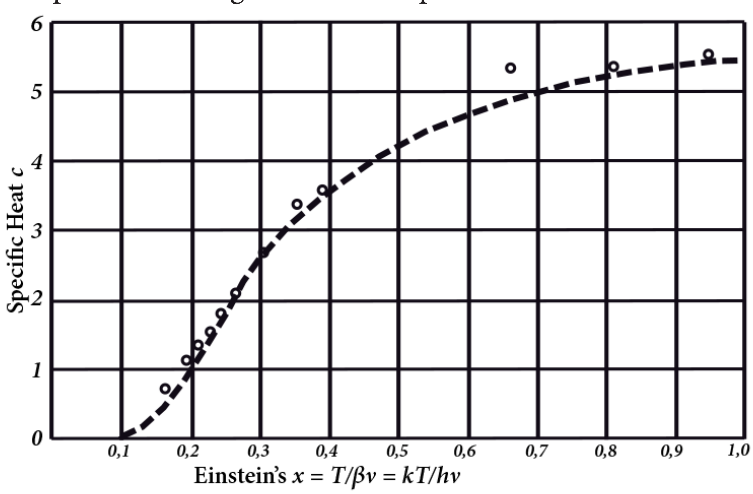


Figure 8-8. Einstein's prediction for specific heats.

In 1913, Niels Bohr would identify the internal quantum states of excited electrons as responsible for the spectral lines in atomic hydrogen. This was a direct extension of Einstein's discoveries.

3 CPAE, vol,2, Doc.38, p.220.

Walther Nernst was one of the first physicists to embrace the quantum theory of Einstein. He did not support the light quantum hypothesis. No one but Einstein himself took it seriously for decades, but Nernst accepted Einstein's idea of quantized energy levels in matter as the explanation of the anomalous specific heats.

We saw in chapter 4 that Planck assumed the energy of radiating oscillators was limited to multiples of *hν*, but this was just a lucky guess at a mathematical formula matching the experimental data.

Planck himself did not believe in the *reality* of this hypothesis about quantized energy levels, but Einstein in 1906 showed that the Planck radiation law required such energy levels, and that they explained the specific heat approaching zero for low temperatures.

In 1905 Nernst proposed a radical theory for the specific heats and entropy of liquids and solids at what he called absolute zero. He began a program of detailed measurements of specific heat at extremely low temperatures.

A few years later Nernst announced a postulate that later became known as the "third law" of thermodynamics - the entropy of a perfect crystal at absolute zero (zero degrees Kelvin) is exactly equal to zero. He wrote

> one gains the clear impression that the specific heats become zero or at least take on very small values at very low temperatures. This is in qualitative agreement with the theory developed by Herr Einstein.[4]

Nernst was thus one of the few supporters of Einstein's contributions to quantum theory to appear in the long years from 1905 to 1925. To be sure, it must have been terribly frustrating for Einstein to see his critically important light quantum hypothesis ignored for so long. But the idea that atoms and molecules contained energy levels was about to be taken very seriously (by Bohr in 1913), and Einstein was the first proponent of discrete energy levels.

Nernst organized the first international meeting of scientists that took Einstein's quantum theory seriously. It was financed by the Belgian industrialist Ernst Solvay. The topic of the first Solvay conference, in 1911, was specific heats. Nernst gave Einstein the privilege of being the last speaker. His paper was called "The Current Status of the Specific Heat Problem."

4 Pais, 1982, p.398.

Einstein included a very lengthy recapitulation of all his earlier arguments for the light quantum hypothesis. His paper is twenty-three pages long [5] and is followed by an eleven-page discussion by Poincaré, Lorentz, Wien, Planck, and of course, Einstein and Nernst.

Although Nernst was the earliest supporter of quantum theory, as applied to matter, he was very frank at the first Solvay conference that it still needed a lot of experimental research.

> At this time, the quantum theory is essentially a computational rule, one may well say a rule with most curious, indeed grotesque, properties. However,...it has borne such rich fruits in the hands of Planck and Einstein that there is now a scientific obligation to take a stand in its regard and to subject it to experimental test. [6]

Unfortunately, Einstein did no more work on quantum theory for the next five years as he focused all his energy on publishing his general theory of relativity.

As Abraham Pais said, one hopes that Einstein got some small satisfaction from the fact that his work on the specific heats of solids was a step in the right direction. He deserves the title of first solid state physicist. But as he wrote to a friend in 1912, Einstein was at least as puzzled as he was pleased with his ideas about specific heat,

> In recent days, I formulated a theory on this subject. *Theory* is too presumptuous a word — it is only a groping without correct foundations. The more success the quantum theory has, the sillier it looks. How nonphysicists would scoff if they were able to follow the course of its development. [7]

Albert Messiah's classic text makes Einstein's contribution clear.

> Historically, the first argument showing the necessity of "quantizing" material systems was presented by Einstein in the theory of the specific heat of solids (1907). [8]

Nernst and others extended Einstein's ideas on specific heat to liquids, but made no progress with gases at temperature absolute zero. That problem had to wait for nearly two decades and Einstein's discovery of quantum statistics. See chapter 15.

5 CPAE, vol 3, Doc.26.
6 Pais, 1982, p.399.
7 Pais, *ibid*.
8 Messiah, 1961, p.21