Superconductivity: Anatomy of a Discovery

Peter Pesic St. John's College, Santa Fe, NM

with thanks to the John Simon Guggenheim Foundation

Cryogenics timeline

- 1832 Michael Faraday liquefies chlorine
- 1869 Thomas Andrews measures isotherms of CO₂ (critical point)
- 1873 J. D. Van der Waals: $(p + a/v^2)(v b) = RT$
- 1877 Louis Cailletet and Raoul Pictet obtain very small droplets of liquid oxygen
- 1880 Van der Waals: principle of equivalent states
- 1883 Szygmunt Wroblewsky and Karol Olszewski liquefy oxygen
- 1895 William Ramsey discovers terrestrial helium
- 1896 Hampson and Linde obtain patents for liquid air cycle
- 1898 James Dewar liquefies hydrogen
- 1908 Heike Kamerlingh Onnes liquefies helium
- 1911 Onnes and associates discover superconductivity



Michael Faraday's apparatus for the liquefaction of chlorine (1832)



Louis Cailletet's apparatus for the liquefaction of gases



Raoul Pictet's method for the liquefaction of oxygen (1877)



The liquefaction of oxygen by Raoul Pictet (1877)

Cryogenics timeline

- 1832 Michael Faraday liquefies chlorine
- 1869 Thomas Andrews measures isotherms of CO₂ (critical point)
- 1873 J. D. Van der Waals: $(p + a/v^2)(v b) = RT$
- 1877 Louis Cailletet and Raoul Pictet obtain very small droplets of liquid oxygen
- 1880 Van der Waals: principle of equivalent states
- 1883 Szygmunt Wroblewsky and Karol Olszewski liquefy oxygen
- 1895 William Ramsey discovers terrestrial helium
- 1896 Hampson and Linde obtain patents for liquid air cycle
- 1898 James Dewar liquefies hydrogen
- 1908 Heike Kamerlingh Onnes liquefies helium
- 1911 Onnes and associates discover superconductivity



"A Friday Evening Discourse at the Royal Institution: Sir James Dewar on Liquid Hydrogen, 1904," by Henry Jamyn Brooks (Royal Institution)



Sir James Dewar and his famous flask Don't be irascible.

"Golden Ages" of Dutch science

1548-1620: Simon Stevin 1628-49: René Descartes in Holland 1629-95: Christiaan Huygens 1632-1723: Antonie van Leewenhoeck

1901: Jacobus van t' Hoff1902: Hendrik Lorentz and Pieter Zeeman1910: Johannes Didereck van der Waals1913: Heike Kamerlingh Onnes

1984: Simon van der Meer1999: Gerardus t' Hooft and Martinus Veltman



Heike Kamerlingh Onnes (1853-1926)

"It seems to me that nowadays the conviction gains ground that in the present advanced stage of scientific investigation only *that* man can experiment with success who has a wide knowledge of theory and knows how to apply it; on the other hand, only *that* man can theorize with success who as a great experience in practical laboratory work."

Kamerlingh Onnes's preface to his doctoral thesis (1879), quoting Hermann von Helmholtz, "Gustav Magnus In Memoriam" (1871)

Experimenters, study theory! Theorists, study experiment!

Who is your hero? Whom will you quote?



Kamerlingh Onnes and his mentor, Van der Waals

The Law of Corresponding States

"If we express the pressure in terms of the critical pressure, the volume in terms of the critical volume, and the absolute temperature in terms of the absolute critical temperature, the isothermal for all bodies becomes the same.... The result, then, no longer contains any reference to the specific properties of various bodies, the 'specific' has disappeared.... All substances form one single genus."

Van der Waals, The Continuity of the Liquid and Gaseous States (1888)

"And all such mechanical quantities of a substance in an arbitrary state, can be calculated from those observed with the other substance in the corresponding state by the ratio of the derived absolute units, in which these quantities are measured."

Kamerlingh Onnes, "Remark on the Liquefaction of Hydrogen, on Thermodynamical Similarity, and on the use of Vacuum Vessels" (1896)

THÉORIE GÉNÉRALE DE L'ÉTAT FLUIDE

PAR

H. KAMERLINGH ONNES.

(Extrait d'an mémoire publié en 1881 par l'Académie Royale des Sciences d'Amsterdam).

Première partie.

Les considérations développées dans ce travail reposent sur cette hypothèse, que les molécules de tous les corps liquides ou gazeux, auxquels on peut donner le nom général de fluides, sont des corps élastiques *semblables*, dont les dimensions sont sensiblement invariables, et qui s'attirent avec des forces que l'on peut ramener à une pression dans la surface du liquide, pression qui pour une même substance est proportionnelle au carré de la densité. On admettra en outre le théorème de la théorie mécanique de la chaleur, en vertu duquel l'énergie cinétique des molécules, dans leur mouvement de translation, mesure la température de la substance.

La première partie de notre hypothèse peut paraître très risquée et partant stérile. Pour justifier le point de départ que nous avons choisi, nous rappellerons que dans la déduction de la formule de M. van der Waals, dont découlent tant de lois importantes, non seulement la même hypothèse est prise comme base, mais en outre il est tenu compte, d'une façon originale, de l'influence des dimensions des molécules, supposées sphériques, sur le nombre de leurs chocs: on y arrive en diminuant, dans la formule, le volume du fluide d'une quantité constante b. Aussi longtemps que le volume

Kammerlingh Onnes, "General Theory of the Fluid State" (1881)

After

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5} + \frac{G}{v^6} \quad . \quad . \quad (40^\circ \ V)$$

..

were investigated a large number of forms at 40° C.

$$pv = A + \frac{B}{v} + \frac{C}{v(v-\gamma)} + \frac{D}{v(v-\gamma)^2} + \frac{E}{v(v-\gamma)^3} + \frac{F}{v(v-\gamma)^4} \quad . \quad (40^{\circ} I)$$

$$pv = A + \frac{D}{v} + \frac{C}{v(v-\gamma)} + \frac{D}{v(v-\gamma)^3} + \frac{E}{v(v-\gamma)^5} + \frac{F}{v(v-\gamma)^7} \quad . \quad (40^{\circ} II)$$

$$pv = A + \frac{B}{v} + \frac{C}{v(v-\gamma)}e^{v-\gamma} + \frac{D}{v(v-\gamma)^2}e^{\frac{2\gamma}{v-\gamma}} + \frac{D}{v(v-\gamma)^2}e^{v-\gamma} + \frac{D}$$

$$+ \frac{E}{v (v-\gamma)^3} e^{\frac{3\gamma}{v-\gamma}} + \frac{F}{v (v-\gamma)^4} e^{\frac{4\gamma}{v-\gamma}} \cdot \cdot (40^\circ III)$$

$$pv = A + \frac{B}{v} + \frac{C}{v^3} + \frac{D}{v^5} + \frac{E}{v^7} + \frac{F}{v^9}$$
. (40° VI)

$$pv = A + \frac{B}{v} + \frac{C}{v^2}e^{-\frac{v}{\gamma}} + \frac{D}{v^3}e^{-\frac{2v}{\gamma}} + \frac{E}{v^4}e^{-\frac{3v}{\gamma}} + \frac{F}{v^5}e^{-\frac{4v}{\gamma}}$$
(40° VII)

Kammerlingh Onnes, "Expression of the Equation of State of Gases and Liquids by means of Series" (1901)



Resistivity versus temperature for various substances



Resistivity versus temperature for lead and platinum, along with Lord Kelvin's 1902 predictions

"Physics owes its fruitfulness in creating the elements of our material well-being and its enormous influence on our metaphysics to the pure spirit of experimental philosophy. Its primary role in the thoughts and actions of contemporary society can be maintained only if, through observation and experimentation, physics continues to wrest from the unknown ever new territory.

Nevertheless, a large number of institutions are needed for physics to play this role, and they need resources. Both are now woefully insufficient when we consider how important it is to society that physics prosper. As a result, the person who accepts the task of forming future physicists and of managing such institutions must be particularly aggressive in putting forth his ideas about what is really needed to carry out experimental research these days."

Kammerlingh Onnes, Inaugural Lecture as Professor of Experimental Physics in Leiden (1882)

What is your vision of the future of physics?

"Perhaps, like a poet, his work and all his activities are motivated solely by a thirst for truth; to penetrate the nature of matter might be his principal goal in life.... What I believe is that quantitative research, establishing relationships between measured phenomena, must be the primary activity of experimental physics. **FROM MEASUREMENT TO KNOWLEDGE** [*Door meten tot weten*] is a motto that I want to see engraved on the door of every physics laboratory."

Kammerlingh Onnes, Inaugural Lecture as Professor of Experimental Physics in Leiden (1882)

What is your motto?



Kammerlingh Onnes and his assistant Gerrit Flim with their helium liquefier



"Blue collar boys" in the instrument maker's school set up by Kamerlingh Onnes next to his physics laboratory (1900)



Gilles Holst (1886-1968)



The nested stages of cold liquids surrounding the measurement of mercury resistivity

march an Too plan mostly to bank. A trap Some hill at gecolded & point, Warnet of let a grate the + tobe legent is an welgeller mar it 12 415 good and their Michael but monower Sist Greeker 1 30 accord products as god gendered were. 47 Jampy Bull, winn the our hundright. Comprime Conclose set you do many name later putting 12' recorde arten froming - Bur hand in haft is will be to make mindet Kale Hay make and and . 180 goutraints entry m Everts the Know of Salah is And ton of 19, 2 an queland I tool manhalf the con Molin. 1'4 gurss Welly mighting no I have ado Bu, souther, gelitte, mar uger Gernstate of a more per Marchathe schenkely planen, this some school by and - hubertonce down; male Relichter Contrat gruch place foreid and Tomprater grante 4" hafyna & top propriotan & rutes 21th 14' green conserved to douber 12 (4) 10, For suntrune for White any but bellichter He motor 8. 1 Howbail I sut good 240 mentremette, to Tombet gov Soul blow the Surger shroft our daughter with million Amiden marketter. From regelillon valling there helenning a office 1 Kid on Withamand Mithing and reacher lacher A part rachy Will man to ger departe gen nulfor won hill life light man to triper.

Kamerlingh Onnes' laboratory notebook for 8 April 1911. Box in red shows his observation for the resistance *Kwik nagenoug nul* ["Mercury practically zero"] at 3 K. The next sentence (*Herhaald met goud*) means "repeated with gold." (Courtesy Boerhaave Museum and Dirk van Delft)



Kamerlingh Onnes's figure of resistance (ohms) in mercury versus temperature (K) from his experiments of 26 October 1911





The levitation of a conducting ball above a superconducting loop, first demonstrated by Kamerlingh Onnes in 1914; conceptual drawing by Flim

"Although it is certainly true that quantitative measurements are of great importance, it is a grave error to suppose that the whole of experimental physics can be brought under this heading. We can start measuring only when we know what to measure;: qualitative observation has to precede quantitative measurement, and by making experimental arrangements for quantitative measurements we may even eliminate the possibility of new phenomena appearing."

Henrik B. G. Casimir, Haphazard Reality: Half a Century of Science (1983)

Beware of your own motto.



heat of liquid helium near 2.2 K.



Superfluidity in liquid helium near near 2.2 K, not observed by Kamerlingh Onnes but first observed in 1933.

"Whether you can observe a thing or not depends on the theory which you use. It is the theory which decides what can be observed."

Albert Einstein, quoted by Werner Heisenberg

"You may find agreement with theory: then you have carried out a measurement.

But if you are lucky, you will find disagreement. Then you have done an experiment."

Enrico Fermi

For further reading

Per Dahl, Superconductivity: Its Historical Roots and Development from Mercury to the Ceramic Oxides (AIP, 19920

Dirk van Delft, Freezing Physics: Heike Kamerlingh Onnes and the Quest for Cold (Amsterdam, KNAW 2007)

Kostas Gavroglu and Yorgos Goudaroulis, *Methodological Aspects of the Development of Low Temperature Physics 1881-1956: Concepts out of Context(s)* (Kluwer Academic, 1989)

Jean Matricon and Georges Waysand, The Cold Wars: A History of Superconductivity (Rutgers, 2003)

Kurt Mendelssohn, The Quest for Absolute Zero: The Meaning of Low Temperature Physics (McGraw-Hill, 1966)

Heike Kamerlingh Onnes, *Through Measurement to Knowledge: Selected Papers*, ed. Kostas Gavroglu and Yorgos Goudaroulis (Kluwer Academic, 1991)