

Title: Statistical Mechanics (PHYS 602) - Lecture 8

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URL: <http://pirsa.org/10100027>

Abstract:



Bose Transition

$$n = \text{number of particles per unit volume} = \frac{1}{L^3} \sum_{\mathbf{m}} \frac{1}{-1 + \exp[\beta \{\epsilon(\mathbf{m}) - \mu\}]}$$

Here the sum is over a vector of integers of length three, and the energy is $\epsilon(\mathbf{m}) = \mathbf{m}^2 \hbar^2 / (2ML^2)$, M being the mass of the particle. For a sufficiently large box, there are two qualitatively different contributions to the sum. The term in which $\mathbf{m} = \mathbf{0}$ can be arbitrarily large because μ can be arbitrarily small. The remaining terms contribute to an integral which remains bounded as μ goes to zero. The result is

$$n = \frac{1}{-L^3 \beta \mu} + \int \frac{d\mathbf{p}}{h^3} \frac{1}{-1 + \exp[\beta \{p^2/(2M) - \mu\}]}$$

The integration has a result that goes to zero as T^3 as the temperature goes to zero. If this system is to maintain a non-zero density as T goes to zero, which we believe it can, it can only do so by having the first term on the right become large enough so that a finite proportion of the entire number of particles in the system will fall into the lowest mode. This is believed to be the basic source of superfluidity.

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$$\sum_{\vec{m}} = \int \frac{d^3 p}{(2\pi \hbar)^3} L^3$$

m_x, m_y, m_z

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$$d^3 p = p^2 dp d\Omega$$

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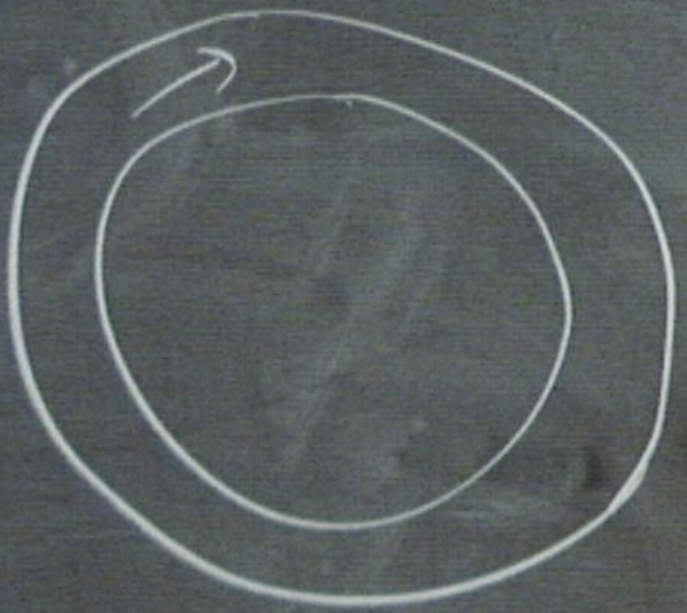
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H-theorem for bosons

Boltzmann equation gives an increasing entropy for bosons of the form of a sum over \mathbf{m} and integral over \mathbf{r} of $-[f \ln f - (1+f) \ln (1+f)]$. Notice how when there is a very large value of f , e.g. when there is macroscopic occupation of a single state, the contribution of this combination turns out to be quite small. The condensed mode does not add appreciably to the entropy.

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m_x, m_y, m_z



$$d^3 p = p^2 dp d\Omega$$

$$= \int \frac{d^3 p}{(2\pi\hbar)^3} f(p) \ln f$$

Dynamics of bosons

Some part of the story of bosons is much the same. A low temperature conserved boson system could be expected to obey the same sort of equation, under circumstances in which the bosons were conserved, and also the emission and absorption of phonons were not too significant.

Specifically, the equation would look like

$$[\partial_t + (\nabla_{\mathbf{p}} \varepsilon) \cdot \nabla_{\mathbf{r}} - (\nabla_{\mathbf{r}} \varepsilon) \cdot \nabla_{\mathbf{p}}] f(\mathbf{p}) =$$

$$- \iiint d\mathbf{q} d\mathbf{p}' d\mathbf{q}' \delta(\mathbf{p} + \mathbf{q} - \mathbf{p}' - \mathbf{q}') \delta(\varepsilon(\mathbf{p}) + \varepsilon(\mathbf{q}) - \varepsilon(\mathbf{p}') - \varepsilon(\mathbf{q}'))$$

$$R(\mathbf{p}, \mathbf{q} \rightarrow \mathbf{p}', \mathbf{q}') [f(\mathbf{p}) f(\mathbf{q})(1 + f(\mathbf{p}')) (1 + f(\mathbf{q}')) - f(\mathbf{p}') f(\mathbf{q}') (1 + f(\mathbf{p})) (1 + f(\mathbf{q}))] \quad \text{vi.9}$$

Once again the new feature is shown in red. In the scattering events there are, for bosons, **more** scattering when the final single particle states are occupied than when they are empty. One says that fermions are unfriendly but bosons are gregarious (or at least attractive to their own tribe.). The f in the $1+f$ term was known in the 19th century in terms of the simulated emission of light, which is a kind of boson. The 20th Century brought **Planck**, and particularly **Einstein**, who first saw the need for the “1” in the $1+f$ term. This extra piece was introduced to make the bose dynamical equation have the right local equilibrium behavior. The logic used by Einstein includes the fact that for local equilibrium via equation vi.9, we must have $f/(-1+f)$ be, as in the fermion case, an exponential in conserved

Landau's equation for low temperature fermion systems:

$$\begin{aligned}
 & [\partial_t + (\nabla_{\mathbf{p}} \epsilon) \cdot \nabla_{\mathbf{r}} - (\nabla_{\mathbf{r}} \epsilon) \cdot \nabla_{\mathbf{p}}] f(\mathbf{p}) = \\
 & - \int \int \int d\mathbf{q} \, d\mathbf{p}' \, d\mathbf{q}' \, \delta(\mathbf{p} + \mathbf{q} - \mathbf{p}' - \mathbf{q}') \, \delta(\epsilon(\mathbf{p}) + \epsilon(\mathbf{q}) - \epsilon(\mathbf{p}') - \epsilon(\mathbf{q}')) \\
 & R(\mathbf{p}, \mathbf{q} \rightarrow \mathbf{p}', \mathbf{q}') [f(\mathbf{p}) f(\mathbf{q}) (1-f(\mathbf{p}')) (1-f(\mathbf{q}')) - f(\mathbf{p}') f(\mathbf{q}') (1-f(\mathbf{p})) (1-f(\mathbf{q}))]
 \end{aligned}$$

We can do just about everything with this equation that Boltzmann did with his more classical result. For example this equation also has an H theorem with H being an integral of $f \ln f + (1-f) \ln(1-f)$. This contribution to minus the entropy goes to zero when f goes to either zero or one.

An important difference from the non-degenerate case is that this equation gives us a particularly low scattering rate at low temperatures. Only modes with energies within kT of the fermi surface can participate in the scattering. As a result, the scattering rate ends up being proportional to T^2 at low temperatures. This low scattering rate guarantees that the excitations with energy $\epsilon(\mathbf{p}, \mathbf{r}, t)$ is stable and can be treated as if it were a particle described by Hamiltonian mechanics. This kind of stable excitation is called a quasi-particle. Quasi-particles are very important in condensed matter physics, particle physics, and many other areas.

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Dynamics of fermions at low temperature

Landau described fermions at low temperature by saying that they had a free energy which depended upon, $f(\mathbf{p}, \mathbf{r}, t)$ the occupations of the fermion modes with momentum in the neighborhood of \mathbf{p} and position in the neighborhood of \mathbf{r} at time t . As the occupations changed the free energy would change by

$$\delta F = \int \frac{d\mathbf{p} d\mathbf{r}}{h^3} \epsilon(\mathbf{p}, \mathbf{r}, t) \delta f(\mathbf{p}, \mathbf{r}, t)$$

Then, using the usual Poisson bracket dynamics the distribution function would obey, as in equation v.13.

$$\partial_t f(\mathbf{p}, \mathbf{r}, t) + (\nabla_{\mathbf{p}} \epsilon(\mathbf{p}, \mathbf{r}, t)) \cdot \nabla_{\mathbf{r}} f(\mathbf{p}, \mathbf{r}, t) - (\nabla_{\mathbf{r}} \epsilon(\mathbf{p}, \mathbf{r}, t)) \cdot \nabla_{\mathbf{p}} f(\mathbf{p}, \mathbf{r}, t) \\ = \text{collision term}$$

The collision term will be the same as in the classical Boltzmann equation with one important difference: Since fermions cannot enter an occupied state, the probabilities of entering a final state will be multiplied by a factor of $(1-f)$. Thus, Landau proposed a “Boltzmann equation” for degenerate fermions of the form below, **with the new terms in red**

$$[\partial_t + (\nabla_{\mathbf{p}} \epsilon) \cdot \nabla_{\mathbf{r}} - (\nabla_{\mathbf{r}} \epsilon) \cdot \nabla_{\mathbf{p}}] f(\mathbf{p}) =$$

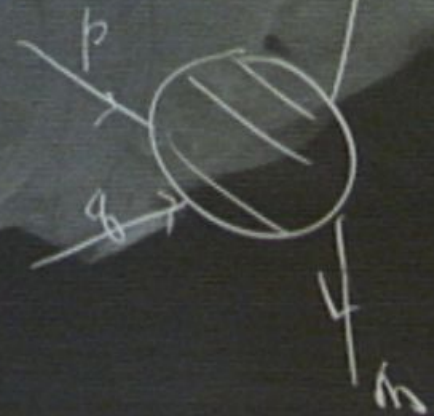
$$- \iiint d\mathbf{q} \, d\mathbf{p}' \, d\mathbf{q}' \, \delta(\mathbf{p} + \mathbf{q} - \mathbf{p}' - \mathbf{q}') \, \delta(\epsilon(\mathbf{p}) + \epsilon(\mathbf{q}) - \epsilon(\mathbf{p}') - \epsilon(\mathbf{q}'))$$

$$\boxed{1} = \sum_{l=0, \infty, \infty} = \int \frac{dp}{(2\pi\hbar)^3} \langle M \rangle$$



$$d\vec{r} = p^2 dp d\Omega$$

$$= \int \frac{dp}{(2\pi\hbar)^3} f(p) \ln f(p)$$



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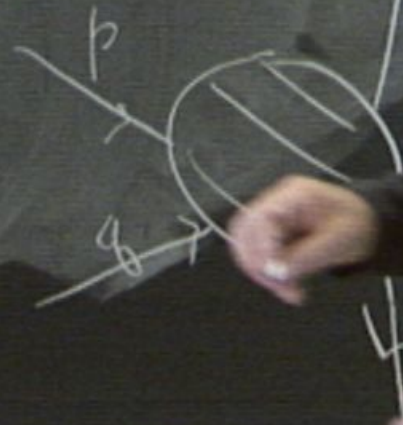
Bose
photons

$$N = \sum_{\vec{m}, m_x, m_y, m_z} = \int \frac{d^3p}{(2\pi\hbar)^3} \langle N \rangle$$



$$d^3p = p^2 dp$$

$$= \int \frac{d^3p}{(2\pi\hbar)^3} f(p)$$



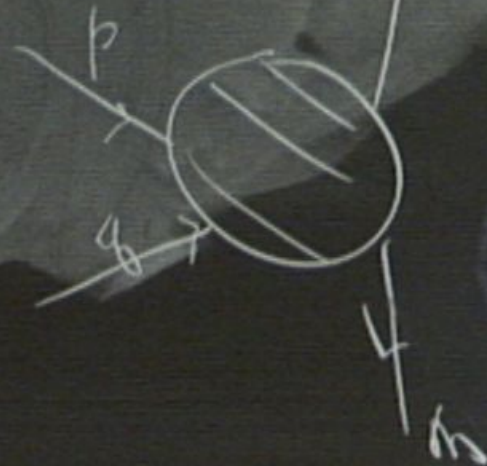
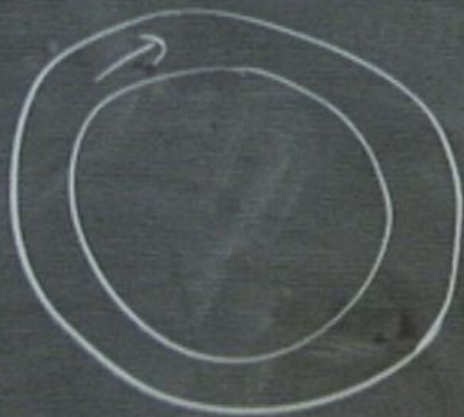
Bose
photons

electrodynamics

$$\langle N \rangle = \sum_{m_1, m_2, m_3} = \int \frac{d^3p}{(2\pi\hbar)^3} \langle N_{\vec{p}} \rangle$$

$$d^3p = p^2 dp d\Omega$$

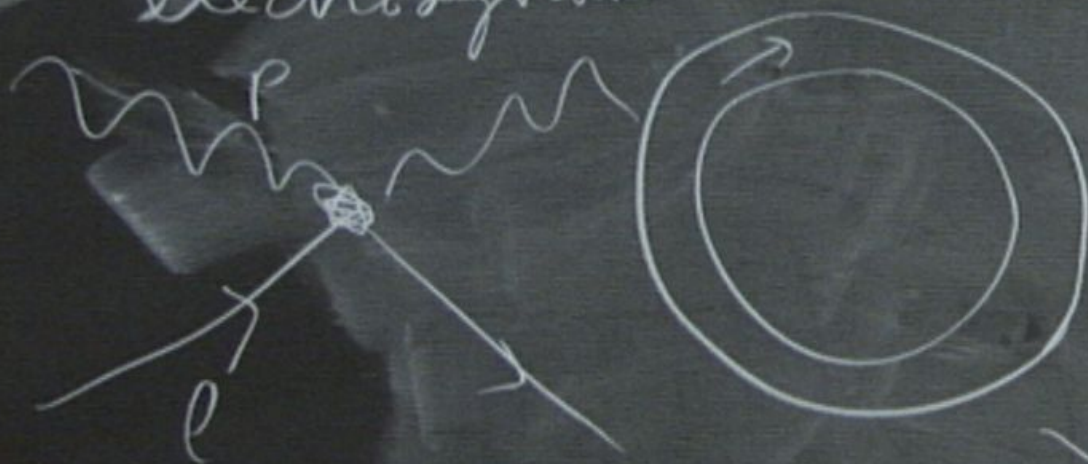
$$= \int \frac{d^3p}{(2\pi\hbar)^3} f(p) \ln f(p)$$



Bose
 photons

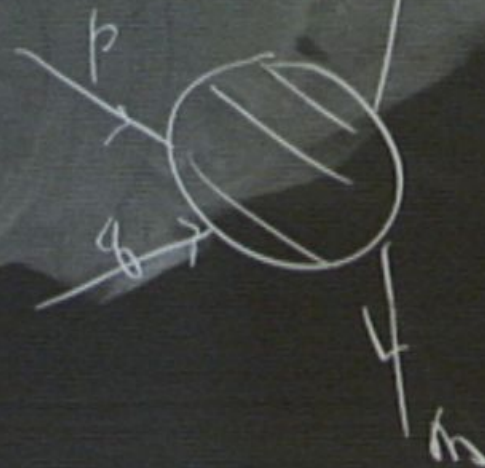
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electrodynamics



$$d\vec{p} = p^2 dp d\Omega$$

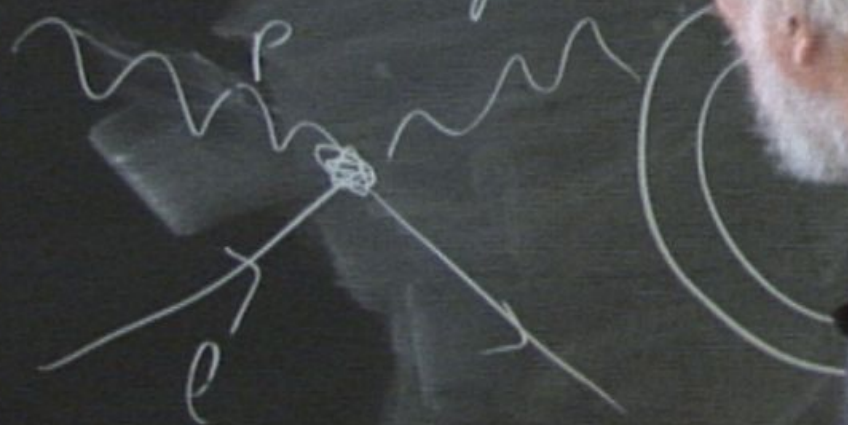
$$= \int \frac{dp}{(2\pi\hbar)^3} f(p) \ln f(p)$$



Bose
 photons

$$N = \sum_m = \int \frac{d^3p}{(2\pi\hbar)^3} \langle N_m \rangle$$

electrodynamics



$$d^3p = p^2 dp d\Omega$$

$$\int \frac{d^3p}{(2\pi\hbar)^3} f(p) \ln f(p)$$



Bose
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electrodynamics

$$Z = \sum_m = \int \frac{d\mu}{(2\pi i)^N} \langle N \rangle$$

m_1, m_2, m_3



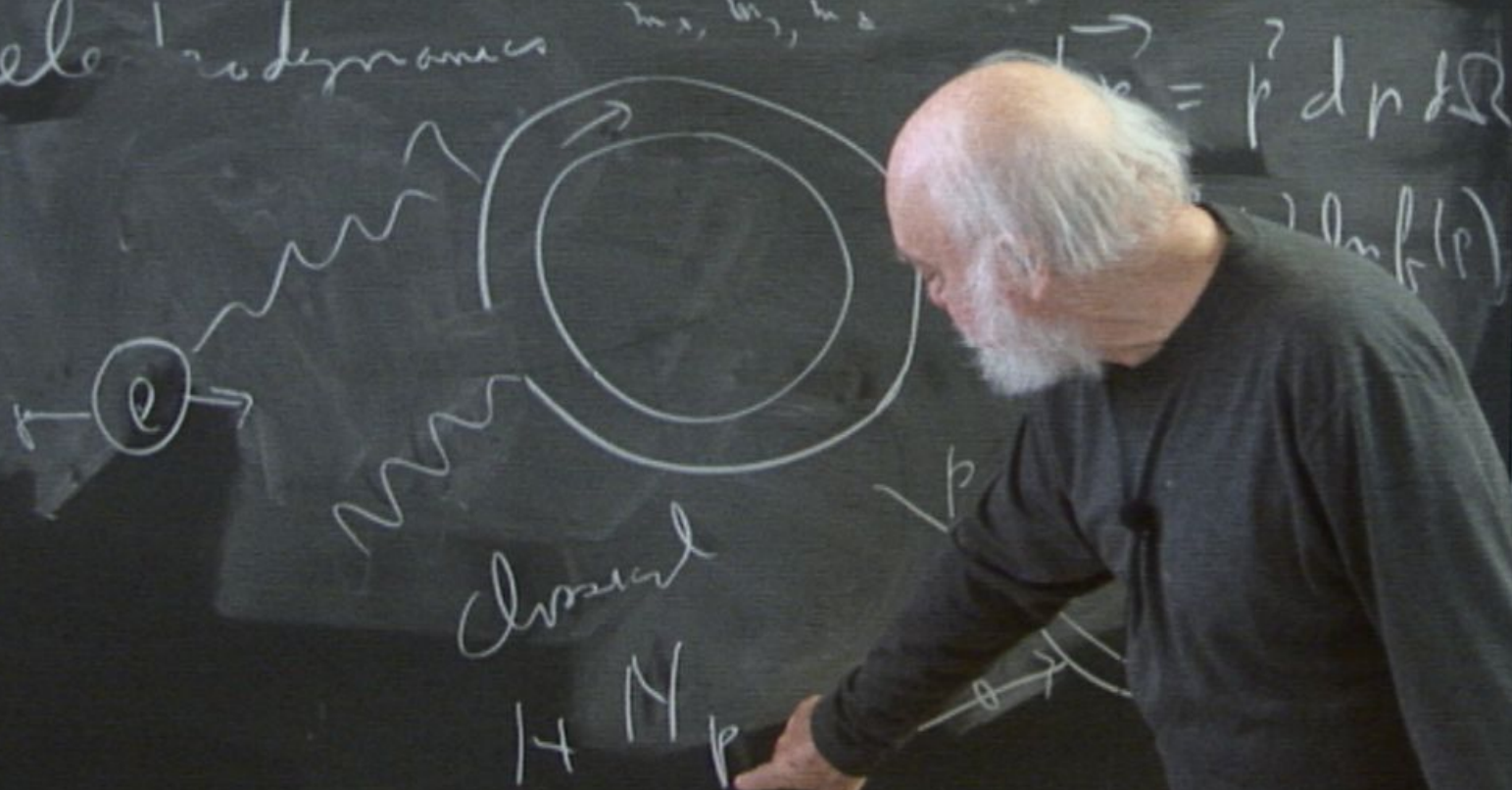
$$p^2 d\mu d\Omega$$

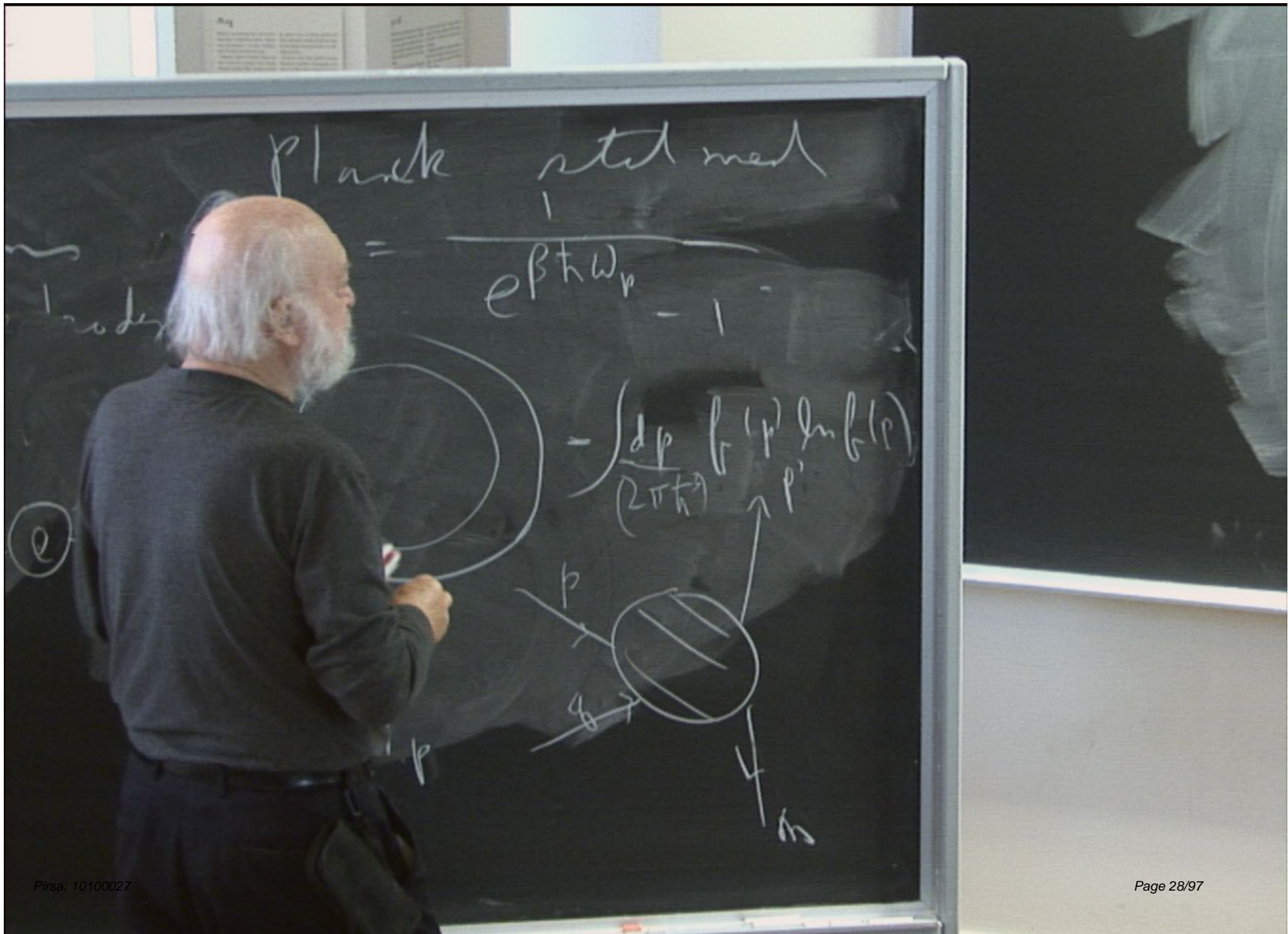
$$p' \ln f(p)$$

Bose
photon
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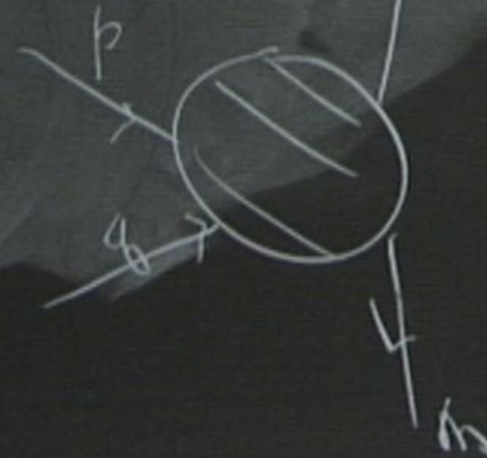


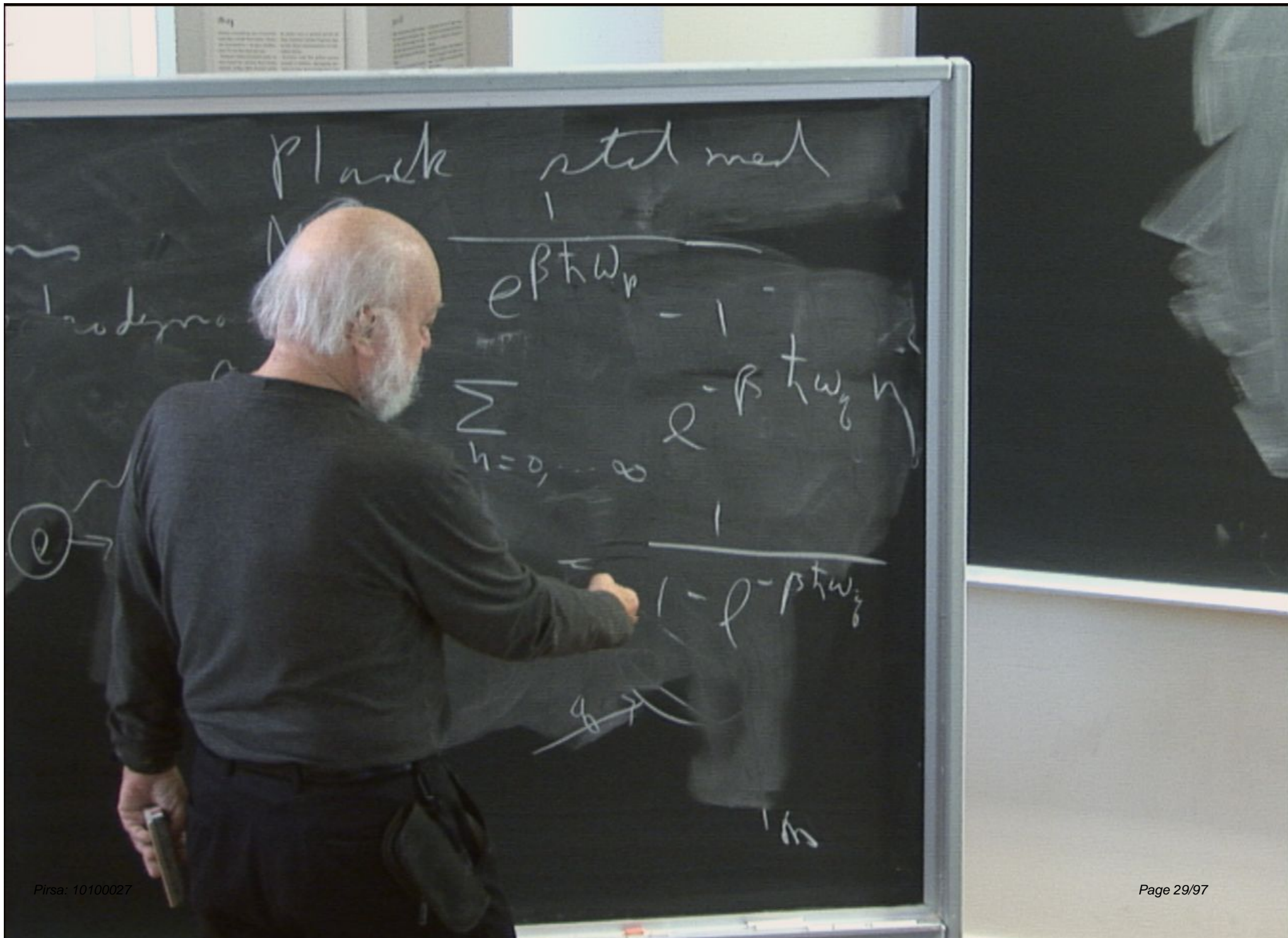
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$$\tilde{\rho} = \frac{1}{e^{\beta H} \Omega_p - 1}$$

$$- \int \frac{dp}{(2\pi\hbar)} f(p) \ln f(p)$$

②





derivation of equilibrium $f(p)$ from Boltzmann equation

equation has

$$\{f(\mathbf{p}) f(\mathbf{q})(1-f(\mathbf{p}')) (1-f(\mathbf{q}')) - f(\mathbf{p}') f(\mathbf{q}') (1-f(\mathbf{p})) (1-f(\mathbf{q}))\}$$

divide through by all $1-f$'s. After division $\{ \}$ becomes

$$\{f(\mathbf{p}) f(\mathbf{q})/[(1-f(\mathbf{p})) (1-f(\mathbf{q}))] - f(\mathbf{p}') f(\mathbf{q}')/[(1-f(\mathbf{p}')) (1-f(\mathbf{q}'))]\}$$

by previous argument this difference vanishes when

$f(\mathbf{p})/(1-f(\mathbf{p})) = \exp[-\beta[\epsilon_{\mathbf{p}} - \mu + \mathbf{p} \cdot \mathbf{v}]]$ so that we get the familiar fermion expression

$$f(\mathbf{p}) = 1/\{\exp[-\beta[\epsilon_{\mathbf{p}} - \mu + \mathbf{p} \cdot \mathbf{v}]] + 1\}$$

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$$\{f(\mathbf{p}) f(\mathbf{q})(1-f(\mathbf{p}'))(1-f(\mathbf{q}')) - f(\mathbf{p}') f(\mathbf{q}') (1-f(\mathbf{p})) (1-f(\mathbf{q}))\} = 0$$

divide through by all $1-f$'s. After division $\{ \}$ becomes

$$\{f(\mathbf{p}) f(\mathbf{q}) / [(1-f(\mathbf{p})) (1-f(\mathbf{q}))] - f(\mathbf{p}') f(\mathbf{q}') / [(1-f(\mathbf{p}')) (1-f(\mathbf{q}'))]\}$$

by previous argument this difference vanishes when

$$f(\mathbf{p}) / (1-f(\mathbf{p})) = \exp[-\beta[\epsilon_{\mathbf{p}} - \mu + \mathbf{p} \cdot \mathbf{v}]] \quad \text{so that we get the familiar fermi}$$

$$f(\mathbf{p}) = 1 / \{\exp[-\beta[\epsilon_{\mathbf{p}} - \mu + \mathbf{p} \cdot \mathbf{v}]] + 1\}$$

Landau's equation for low temperature fermion systems:

$$\begin{aligned}
 & [\partial_t + (\nabla_{\mathbf{p}} \epsilon) \cdot \nabla_{\mathbf{r}} - (\nabla_{\mathbf{r}} \epsilon) \cdot \nabla_{\mathbf{p}}] f(\mathbf{p}) = \\
 & - \iiint d\mathbf{q} \, d\mathbf{p}' \, d\mathbf{q}' \, \delta(\mathbf{p} + \mathbf{q} - \mathbf{p}' - \mathbf{q}') \, \delta(\epsilon(\mathbf{p}) + \epsilon(\mathbf{q}) - \epsilon(\mathbf{p}') - \epsilon(\mathbf{q}')) \\
 & R(\mathbf{p}, \mathbf{q} \rightarrow \mathbf{p}', \mathbf{q}') [f(\mathbf{p}) f(\mathbf{q}) (1-f(\mathbf{p}')) (1-f(\mathbf{q}')) - f(\mathbf{p}') f(\mathbf{q}') (1-f(\mathbf{p})) (1-f(\mathbf{q}))]
 \end{aligned}$$

We can do just about everything with this equation that Boltzmann did with his more classical result. For example this equation also has an H theorem with H being an integral of $f \ln f + (1-f) \ln(1-f)$. This contribution to minus the entropy goes to zero when f goes to either zero or one.

An important difference from the non-degenerate case is that this equation gives us a particularly low scattering rate at low temperatures. Only modes with energies within kT of the fermi surface can participate in the scattering. As a result, the scattering rate ends up being proportional to T^2 at low temperatures. This low scattering rate guarantees that the excitations with energy $\epsilon(\mathbf{p}, \mathbf{r}, t)$ is stable and can be treated as if it were a particle described by Hamiltonian mechanics. This kind of stable excitation is called a quasi-particle. Quasi-particles are very important in condensed matter physics, particle physics, and many other areas.

This approach gives us a piece of a theory of He^3 , the fermion form of helium. To complete the theory one should also consider the emission and absorption of phonons, i.e. sound wave excitations

Landau's equation for low temperature fermion systems:

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 & R(\mathbf{p}, \mathbf{q} \rightarrow \mathbf{p}', \mathbf{q}') [f(\mathbf{p}) f(\mathbf{q}) (1-f(\mathbf{p}')) (1-f(\mathbf{q}')) - f(\mathbf{p}') f(\mathbf{q}') (1-f(\mathbf{p})) (1-f(\mathbf{q}))]
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This approach gives us a piece of a theory of He^3 , the fermion form of helium. To complete the theory one should also consider the emission and absorption of phonons, i.e. sound wave excitations.

Dynamics of bosons

Some part of the story of bosons is much the same. A low temperature conserved boson system could be expected to obey the same sort of equation, under circumstances in which the bosons were conserved, and also the emission and absorption of phonons were not too significant.

Specifically, the equation would look like

$$[\partial_t + (\nabla_{\mathbf{p}} \epsilon) \cdot \nabla_{\mathbf{r}} - (\nabla_{\mathbf{r}} \epsilon) \cdot \nabla_{\mathbf{p}}] f(\mathbf{p}) =$$

$$- \iiint d\mathbf{q} \, d\mathbf{p}' \, d\mathbf{q}' \, \delta(\mathbf{p} + \mathbf{q} - \mathbf{p}' - \mathbf{q}') \, \delta(\epsilon(\mathbf{p}) + \epsilon(\mathbf{q}) - \epsilon(\mathbf{p}') - \epsilon(\mathbf{q}'))$$

$$R(\mathbf{p}, \mathbf{q} \rightarrow \mathbf{p}', \mathbf{q}') [f(\mathbf{p}) f(\mathbf{q})(1 + f(\mathbf{p}')) (1 + f(\mathbf{q}')) - f(\mathbf{p}') f(\mathbf{q}') (1 + f(\mathbf{p})) (1 + f(\mathbf{q}))] \quad \text{vi.9}$$

Once again the new feature is shown in red. In the scattering events there are, for bosons, **more** scattering when the final single particle states are occupied than when they are empty. One says that fermions are unfriendly but bosons are gregarious (or at least attractive to their own tribe.). The f in the $1+f$ term was known in the 19th century in terms of the simulated emission of light, which is a kind of boson. The 20th Century brought **Planck**, and particularly **Einstein**, who first saw the need for the “1” in the $1+f$ term. This extra piece was introduced to make the bose dynamical equation have the right local equilibrium behavior. The logic used by Einstein includes the fact that for local equilibrium via equation vi.9, we must have $f/(-1+f)$ be, as in the fermion case, an exponential in conserved

References

Daniel Kleppner., “Rereading Einstein on Radiation”, *Physics Today*, (February 2005).
A Einstein, *Phys. Z.* **18** 121 (1917). English translation, D. ter Haar, *The Old Quantum Theory*, Pergamon Press, New York, p. 167 (1967).
Louise Gilder “The Age of Entanglement”

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Part 6 Boson-Fermion.key

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References

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Phase Transitions: Scaling, Universality and Renormalization*

Leo P. Kadanoff

The University of Chicago
Chicago, Illinois, USA

and

The Perimeter Institute
Waterloo, Ontario, Canada



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P. A. M. Dirac Proc. Roy. Soc. A 167 148 (1938) renormalization in classical electrodynamics.

might have thought that the new ideas were correct if they had not been so ugly" Dyson quoting Dirac on renormalization.

abstract

In present-day physics, the renormalization method, as developed by **Kenneth G. Wilson**, serves as the primary means for constructing the connections between theories at different length scales. This method is rooted in both particle physics and the theory of phase transitions. It was developed to supplement mean field theories like those developed by **van der Waals** and **Maxwell**, followed by **Landau**.

Sharp phase transitions are necessarily connected with singularities in statistical mechanics, which in turn require infinite systems for their realization. (I call this result the **extended singularity theorem**.) A discussion of this point apparently marked a 1937 meeting in Amsterdam celebrating van der Waals.

Mean field theories neither demand nor employ spatial infinities in their descriptions of phase transitions. Another theory is required that weds a breaking of internal symmetries with a proper description of spatial infinities. The renormalization (semi-)group provides such a wedding. Its nature is described. The major ideas surrounding this point of view are described including especially scaling, universality, and the development of connections among different theories.

Who am I?

A condensed matter theorist, with an interest in the history of science, who intends to talk about a subject closely related to condensed matter, but also to the philosophy of science and particle physics. I am not an expert in either of the latter subjects.

condensed matter physics: formulations clear (stat mech, Schrodinger equation, etc.) **goal:** explain amazing variety of nature. Nature = an Onion, exposed layer after layer. We hope to see mathematical and conceptual beauty arise from the mundane.

particle physics: simple results=masses, cross-sections **goal:** seek clear and final (!!) theoretic formulations based upon experiment and observations. Hope to see the mundane arise from the mathematical beauty of a single truth.

Connections in Condensed Matter Physics

Condensed matter physics relates the observable, often macroscopic, properties of liquids, gases, solids and all everyday materials to more microscopic theories, often the quantum theory of atoms and molecules. Since the macroscopic theories are themselves non-trivial, e.g. elasticity, hydrodynamics, the electrodynamics of materials, it follows that condensed matter physics is largely an exercise in connecting different kinds of theories.

Typically this connection involves different length scales

Size of molecule = 10^{-9} meter. Size of laboratory = 5 meter

One of the deepest aspects of this area of science is the existence of different thermodynamic phases, each with qualitatively different properties. E.g., freezing is a sudden qualitative change in which the material abruptly gains rigidity. How can this happen?

All thermodynamic behavior is based on statistical mechanics.

Connections in Particle Physics

Particle physics often wishes to relate its present, phenomenological, theory to a deeper (?) theory at a much shorter or longer length scale. e.g. Connect the standard model to physics at a LHC, unification, or Planck scale.

Previously the search for a final theory has been impeded by ugliness or singularities arising at scales far from observation. These singularities show up directly as infinities in perturbation theory and indirectly as algebraic behavior ($1/|x-y|^p$) in a correlation function

I am going to follow condensed matter physics for the next parts of this talk, but particle physics and condensed matter physics are essentially similar.

Further Connections

Field Theory and Statistical Mechanics are closely connected. A Wick rotation $t \rightarrow i/(kT)$ will take you from one to the other.

Quantum Mechanics and Classical Mechanics are closely connected. Both employ Hamiltonians as basic generators of time development as do Field Theory and Statistical Mechanics.

All four have a dual structure in which terms in the Hamiltonian both describe measurable quantities and equally generate changes in development.

All four have the same structure: Poisson Bracket and Commutator, conjugate variables = p 's and q 's.

I shall talk mostly about statistical mechanics.

STATISTICAL MECHANICS AND SINGULARITIES

Statistical mechanics (defined by **Ludwig Boltzmann** in 1870s) states that the probability for finding a equilibrium system in a volume element $d\gamma$ about a position, γ , in phase (position and momentum) space is equal to $d\gamma \exp[-\beta(H\{\gamma\} - F)]$. Here β is the inverse temperature, $H\{\gamma\}$ the Hamiltonian or energy and F the free energy of the system. The latter is given by the normalization condition

$$\exp[-\beta F] = \int d\gamma \exp[-\beta H\{\gamma\}]$$

where the integral covers all the configurations of the system. Thus the free energy is proportional to a logarithm of a sum (or integral) of exponentials. For a system that is finite in extent, such a sum is always a smooth (real analytic) function of its arguments. Consequently phase transitions, which involve discontinuous changes as parameters like temperature or pressure are varied, can only be found in infinite systems.

...A phase transition appears as a sharp change in the form of thermodynamic functions, as you go from one kind of behavior to another. These sharp changes are mathematical singularities. A singularity will not happen in any finite system, as in a finite liquid. The singularity can (and does) happen in an infinite system. I call this result the **extended singularity theorem**. This theorem has been extensively used, but not really extensively discussed, in the previous literature.

It follows that any proper description of a phase transition requires a theory which makes an explicit use of the infinite size of the system. Most theories constructed before Wilson's renormalization group (1971) fail this test.



<http://blogs.trb.com/news/local/longisland/politics/blog/2008/04/>

swim in liquid water
abrupt change
walk on solid ice

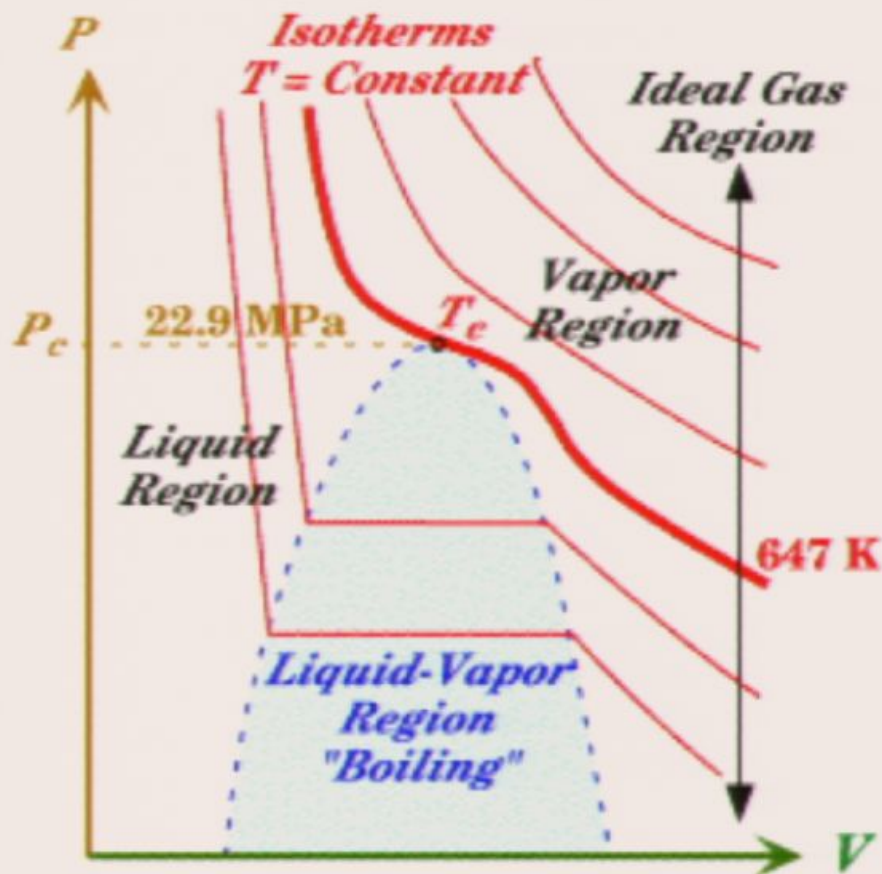


<http://azahar.files.wordpress.com/>

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Phil. Trans. Roy. Soc.
159 p. 575 (1869)



Note qualitative changes.

- as boiling takes one from liquid to vapor
- as one passes from isotherm to isotherm through critical point

These qualitative changes are mathematical singularities.

Cartoon is PVT plot for water, but CO₂ is similar, with a more accessible critical point.

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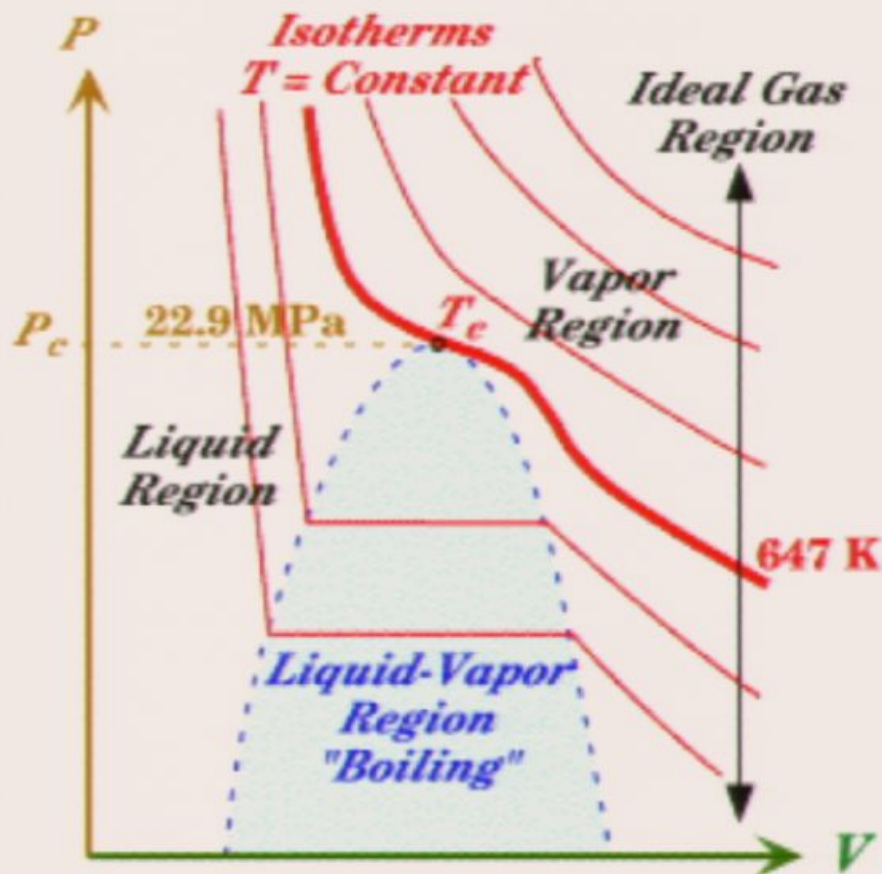


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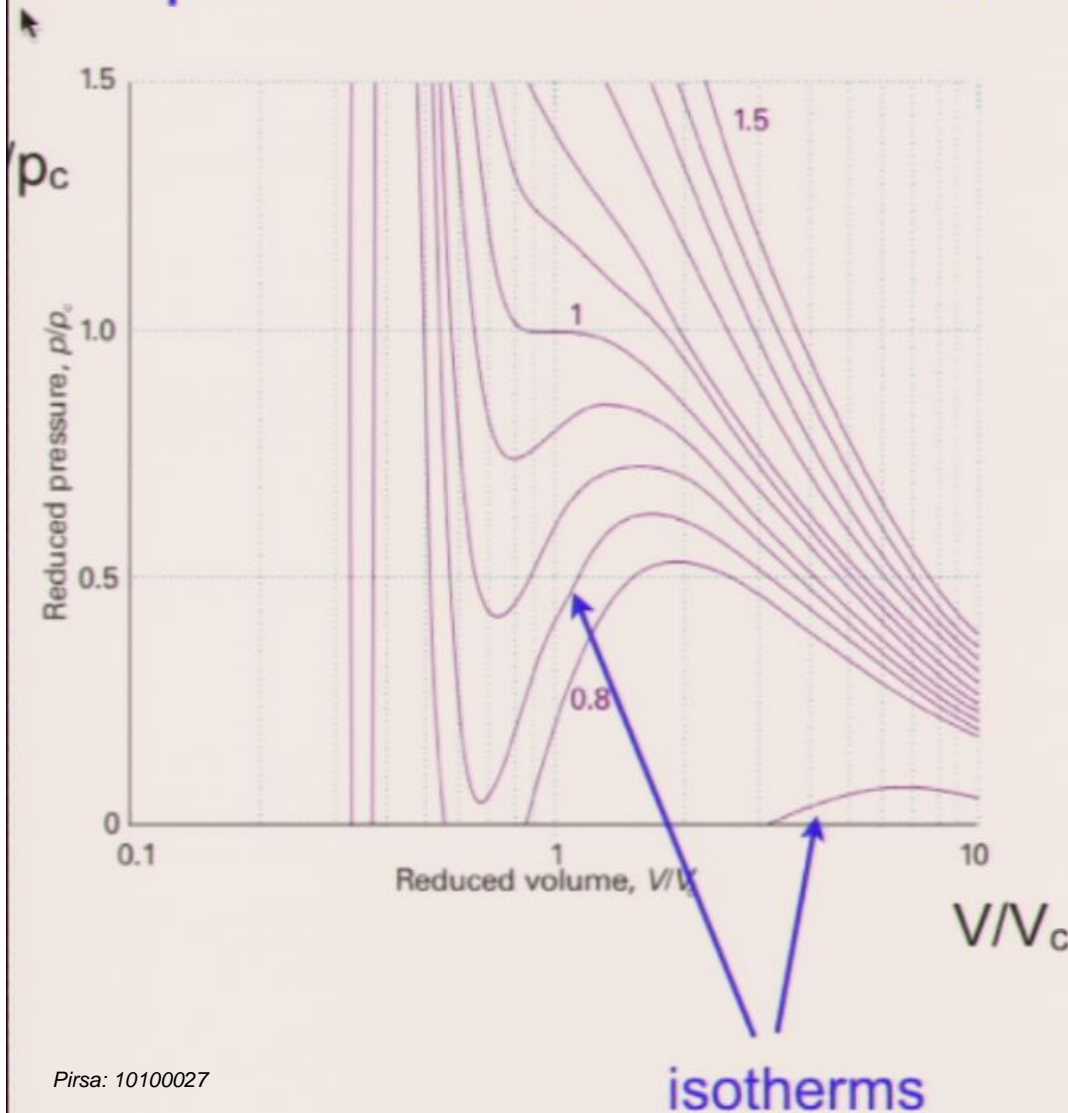
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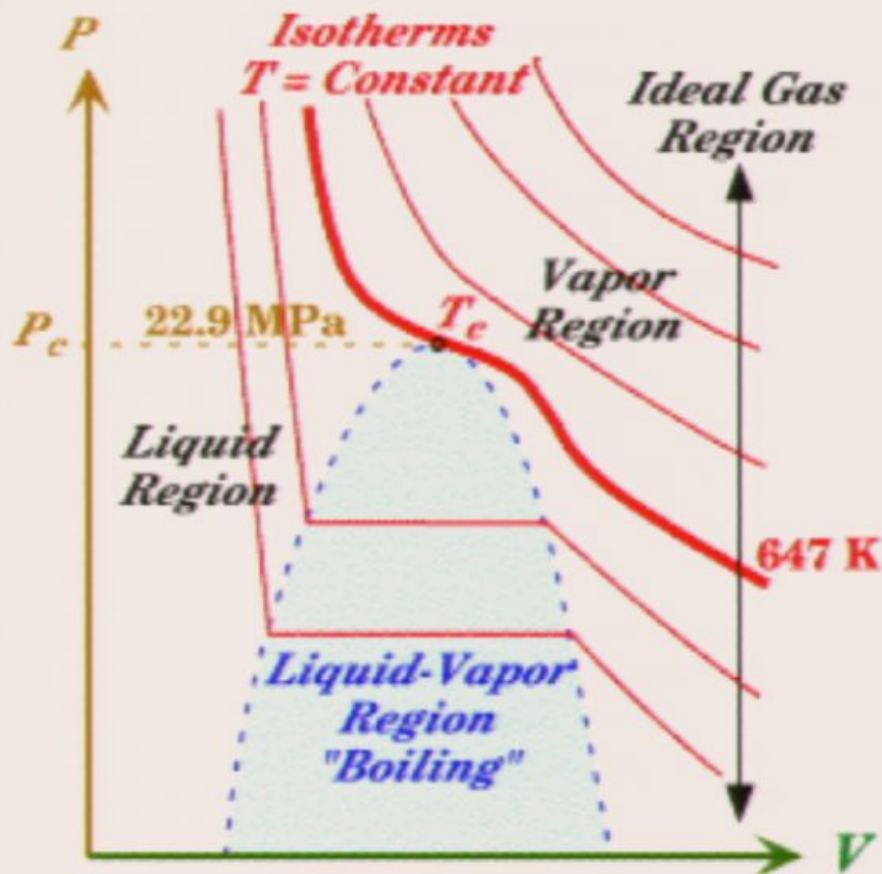
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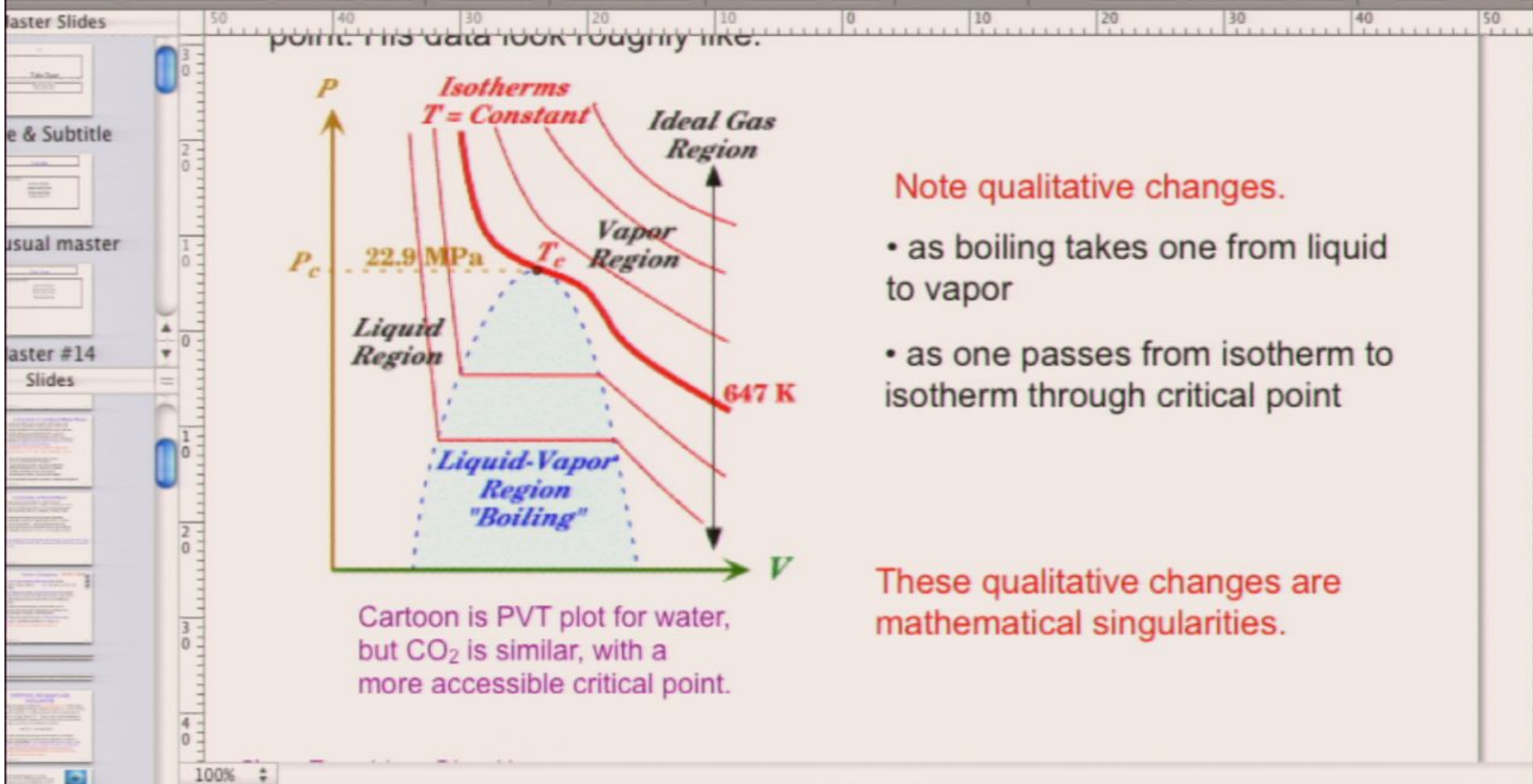


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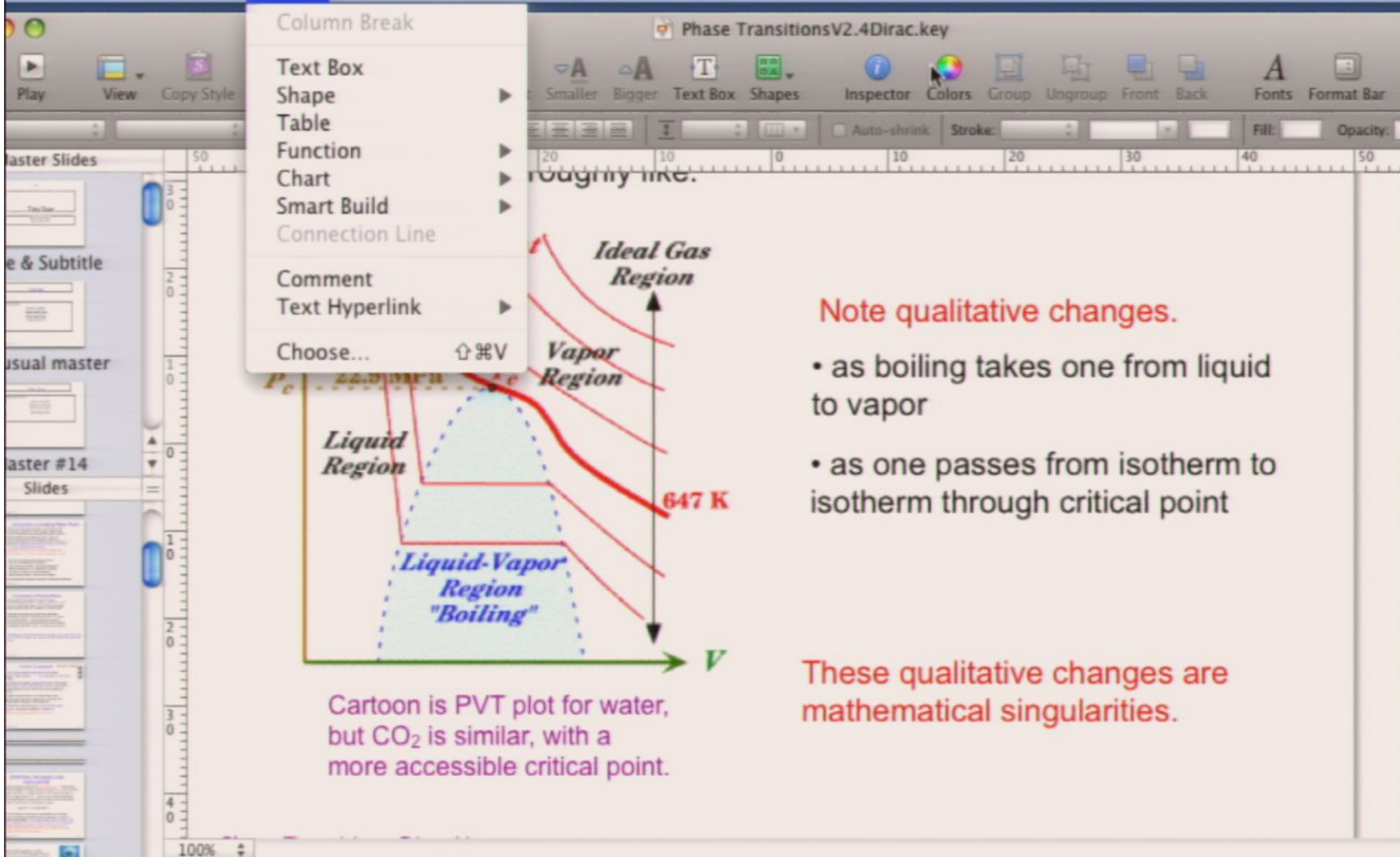
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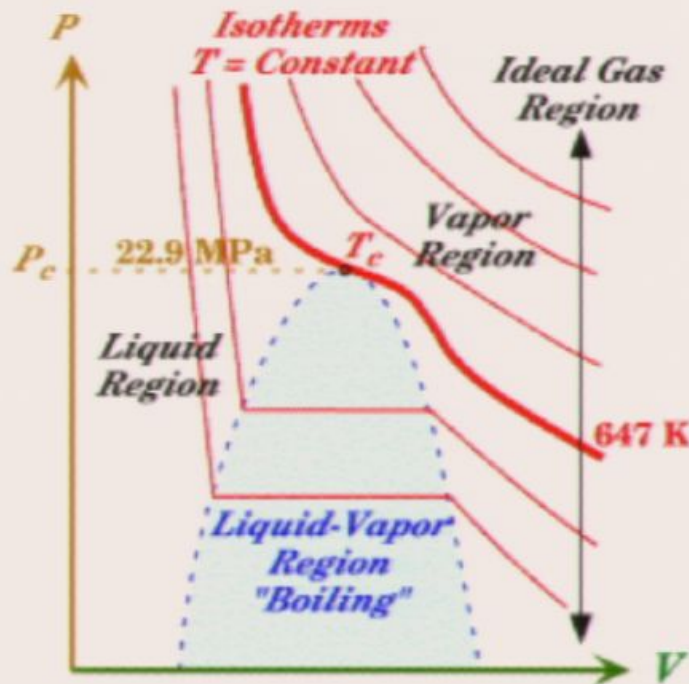
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Ideal Gas Region

Vapor Region

Liquid-Vapor Region "Boiling"

T_c

647 K

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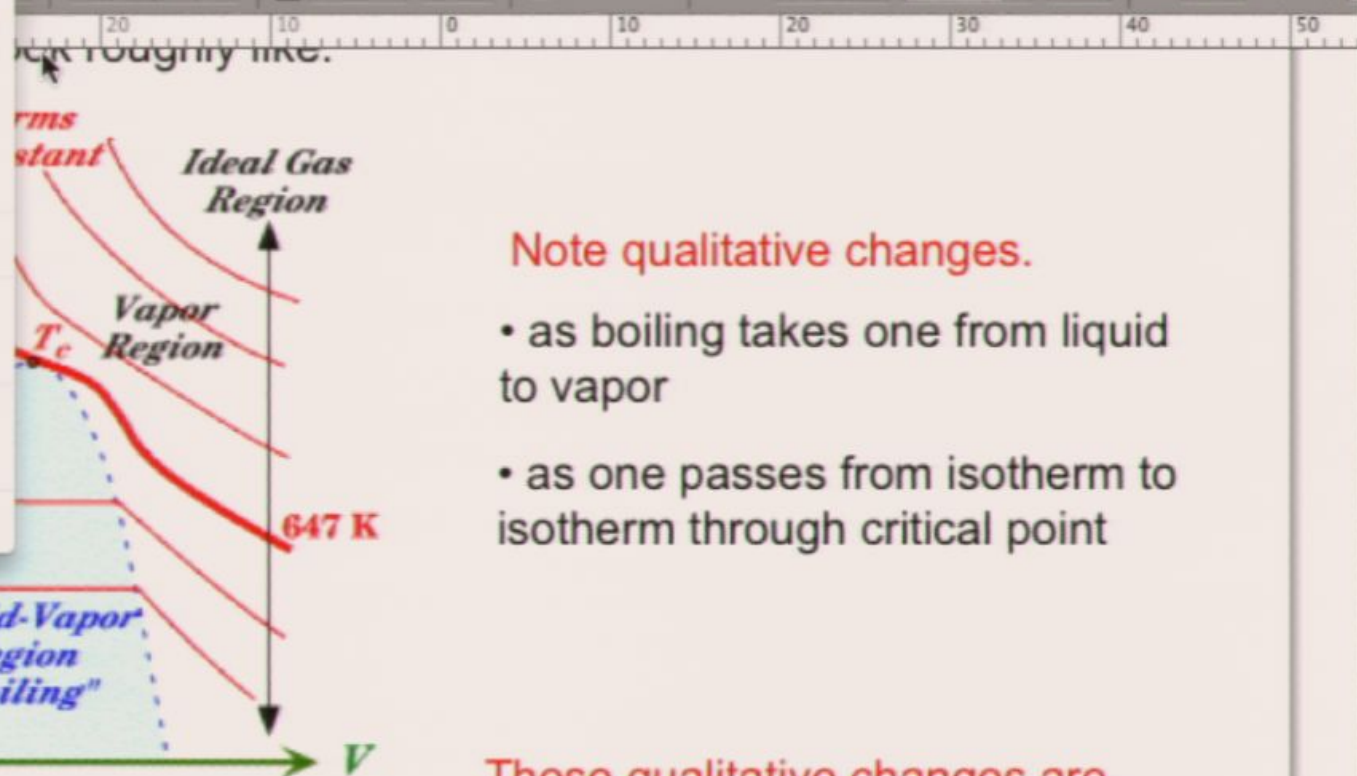
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Part 6 Boson-Fermion.key
Phase TransitionsV2.4Dirac.key — 2010 PSI lectures
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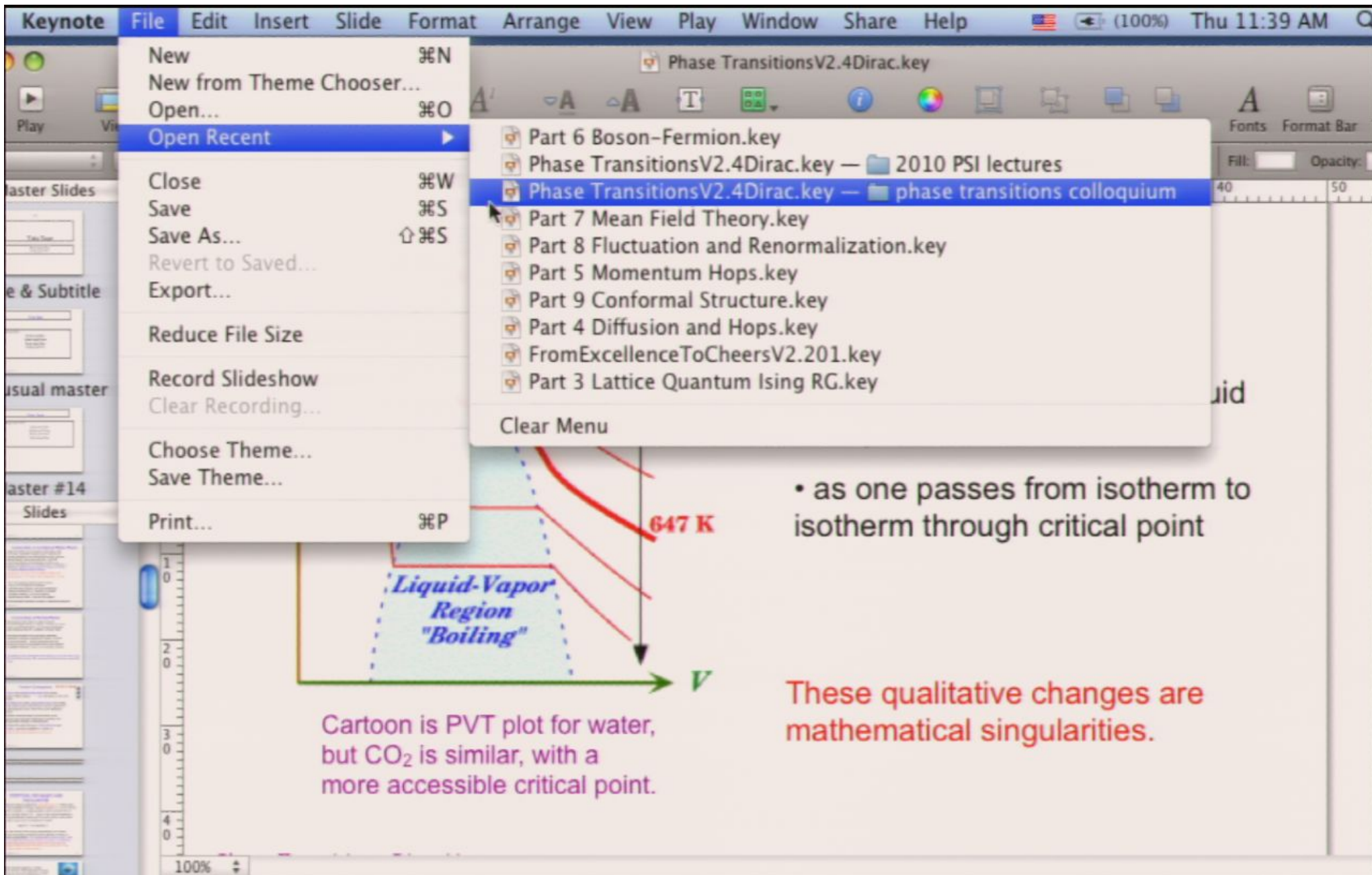
Liquid-Vapor Region "Boiling"

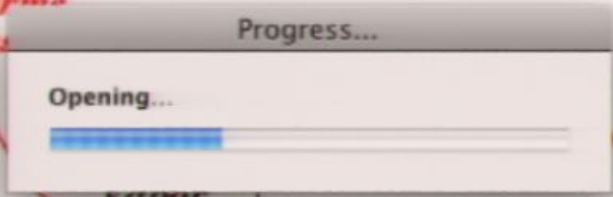
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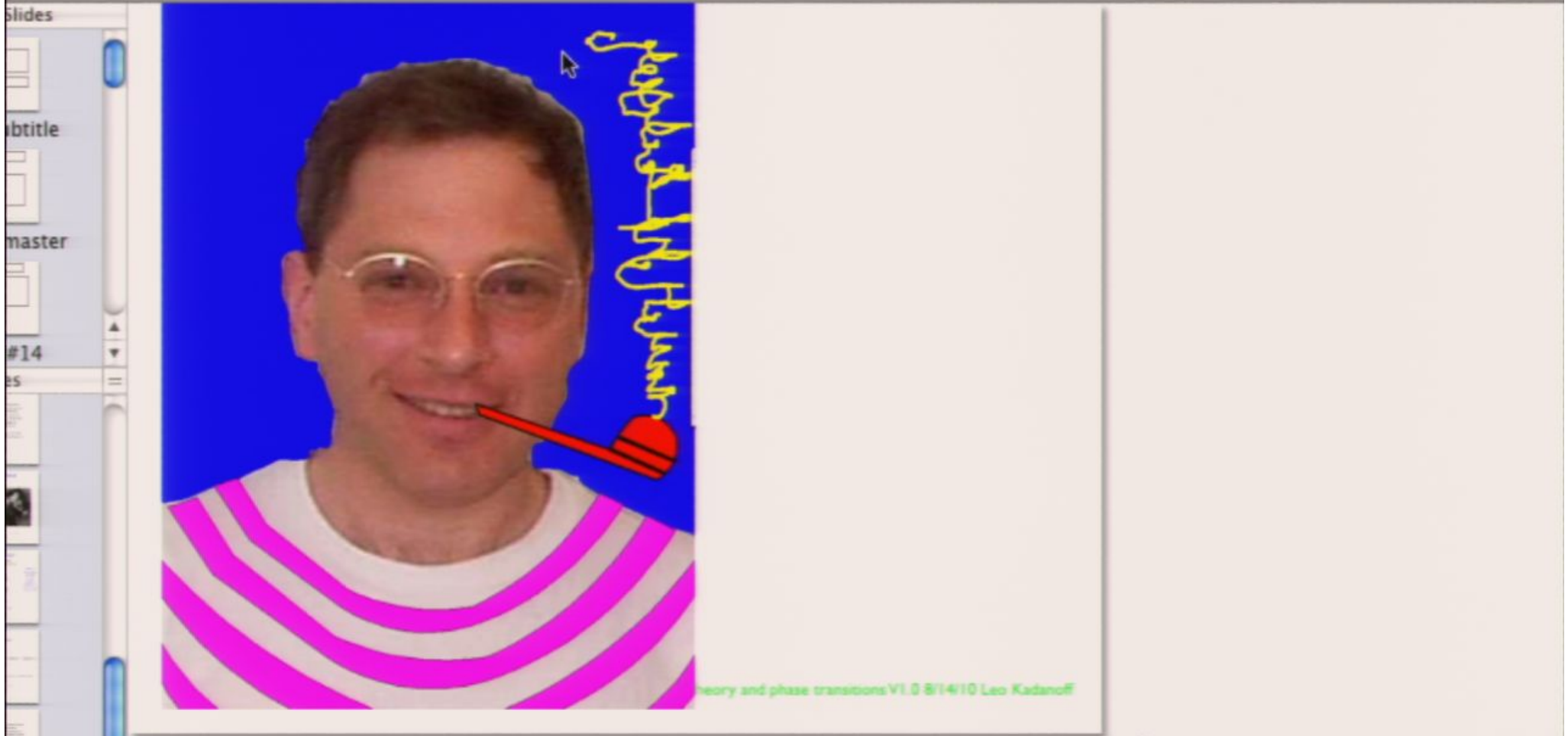




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Part 7 Mean Field Theory.key



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Part 7. Mean Field Theory and Phase Transitions

Materials can exist in quite different phases with quite different properties. Phase transitions describe the change from one phase to another.

The traditional theories of phase transitions are mean field theories, MFT. We shall describe the nature of MFT's by looking particularly at the MFT that applies to the Ising model. Then we shall look at Landau's theory generalizing this work to many different phase transitions.



Perimeter Institute Statistical Physics Lecture Notes Part 7. Mean Field theory and phase transitions V1.0 8/14/10 Leo Kadanoff

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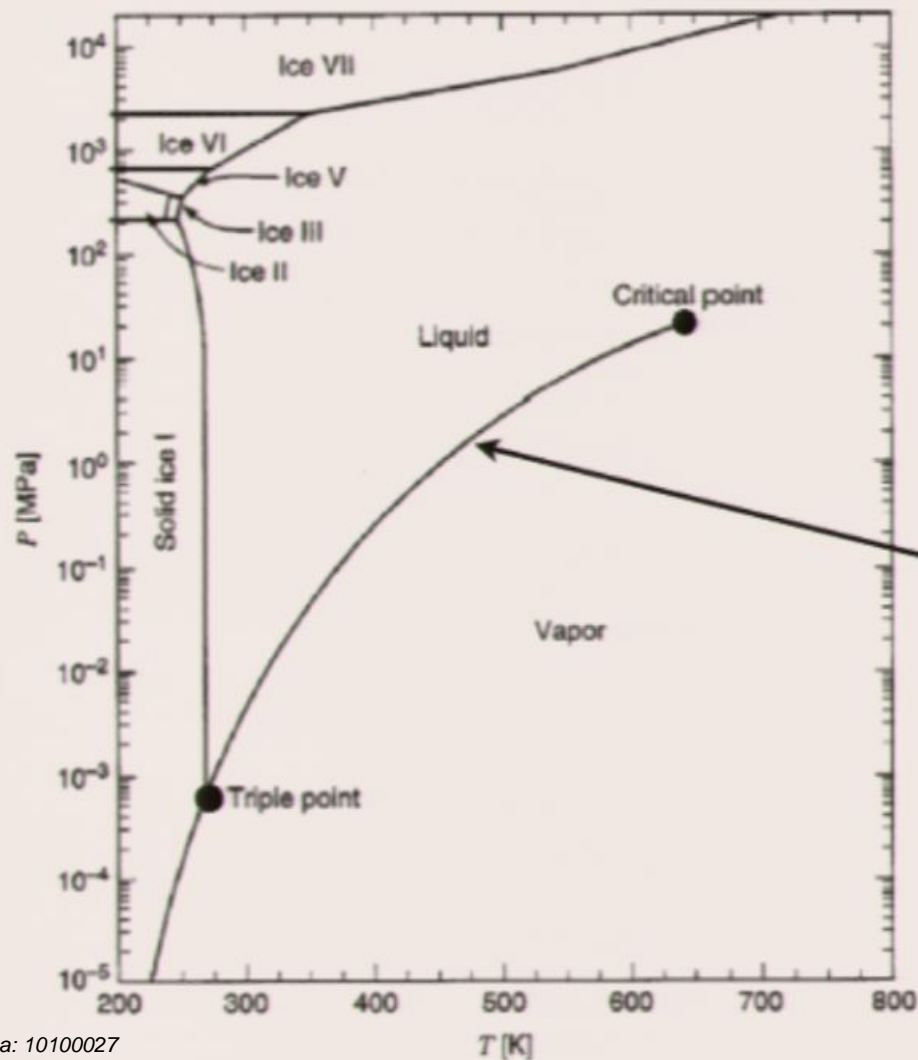
Gibbs: A phase transition is a sharp change in thermodynamic behavior.

Ehrenfest:

- First order phase transition = discontinuous jump in thermodynamic quantities.
- Now we also talk about continuous phase transitions. In these phase transition the system finds itself between two different behaviors. There is no jump in any in thermodynamic quantitie.

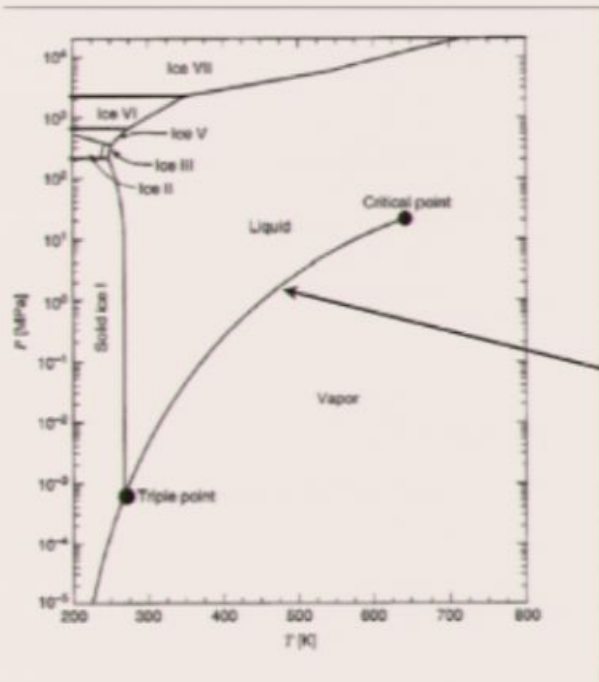


Phase Diagram for Water



liquid-gas phase
transition line

Phase Diagram for Water

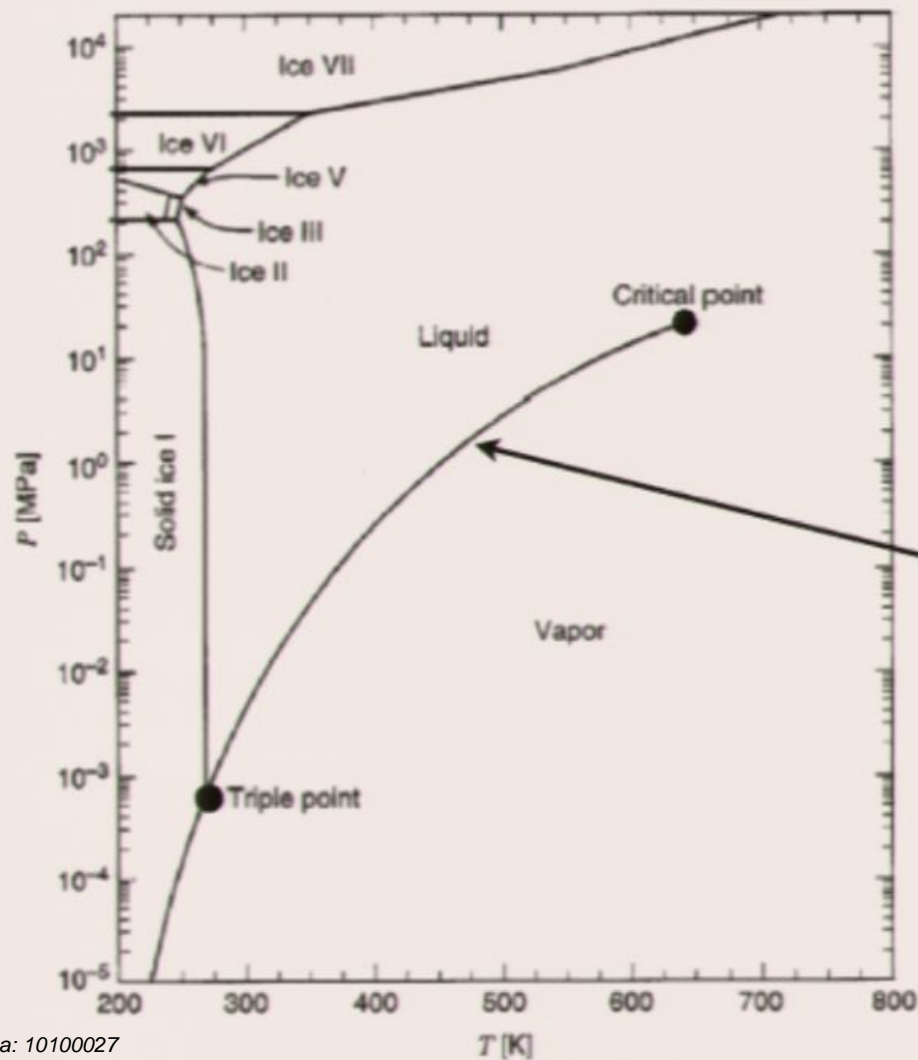


liquid-gas phase transition line

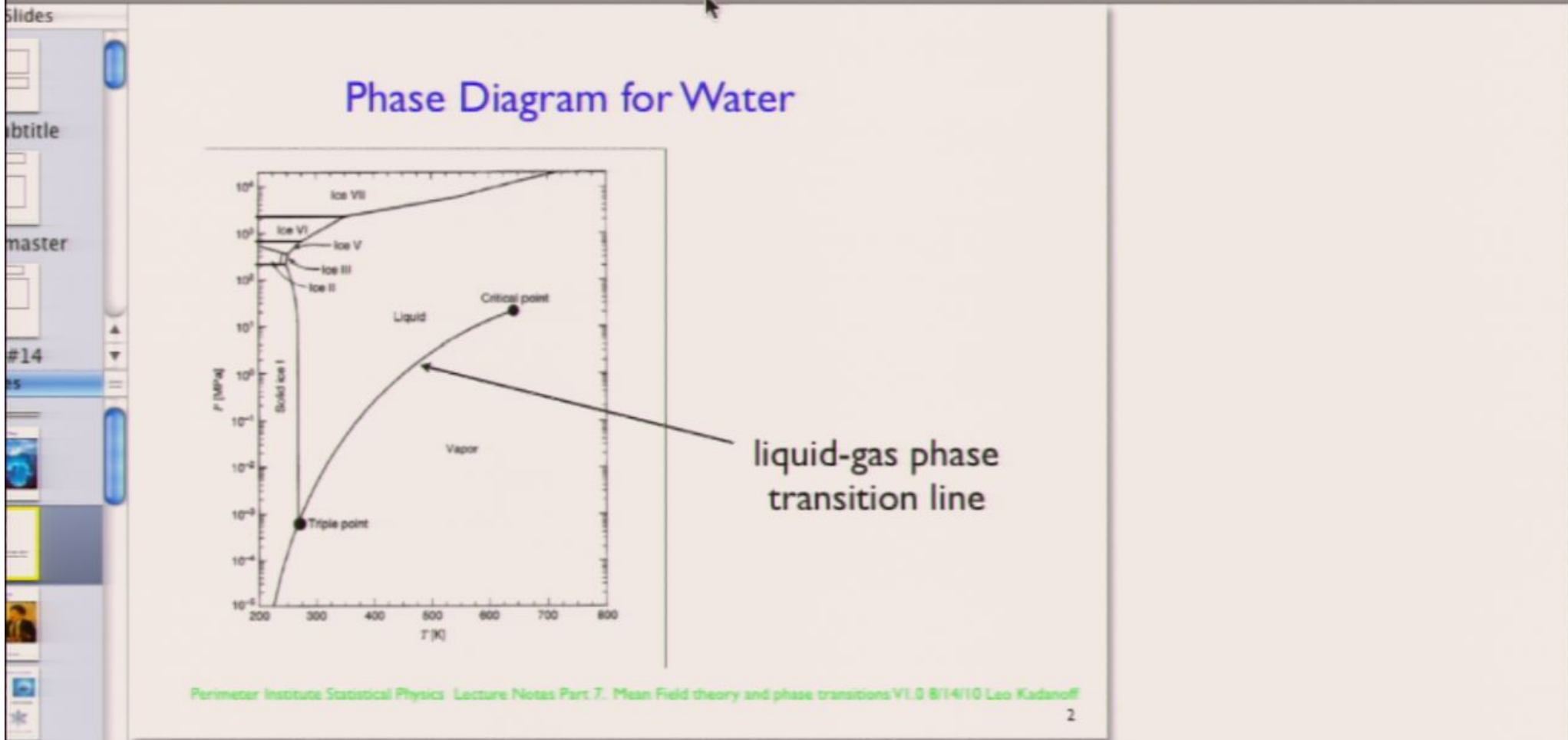
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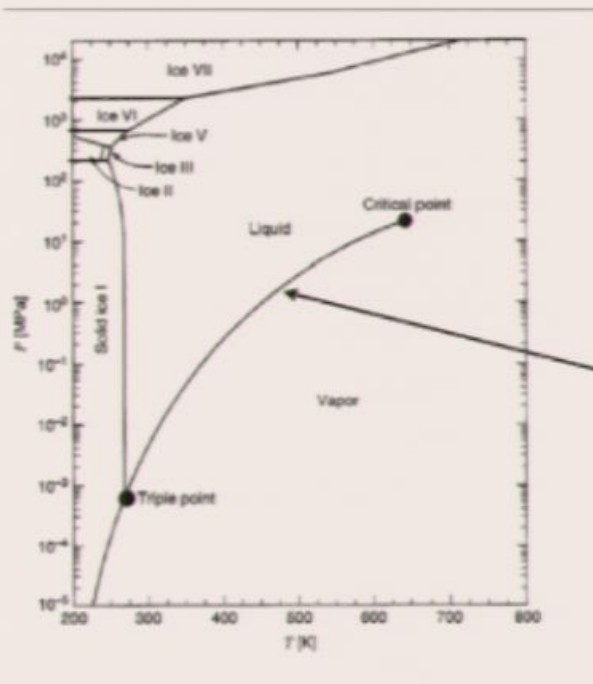
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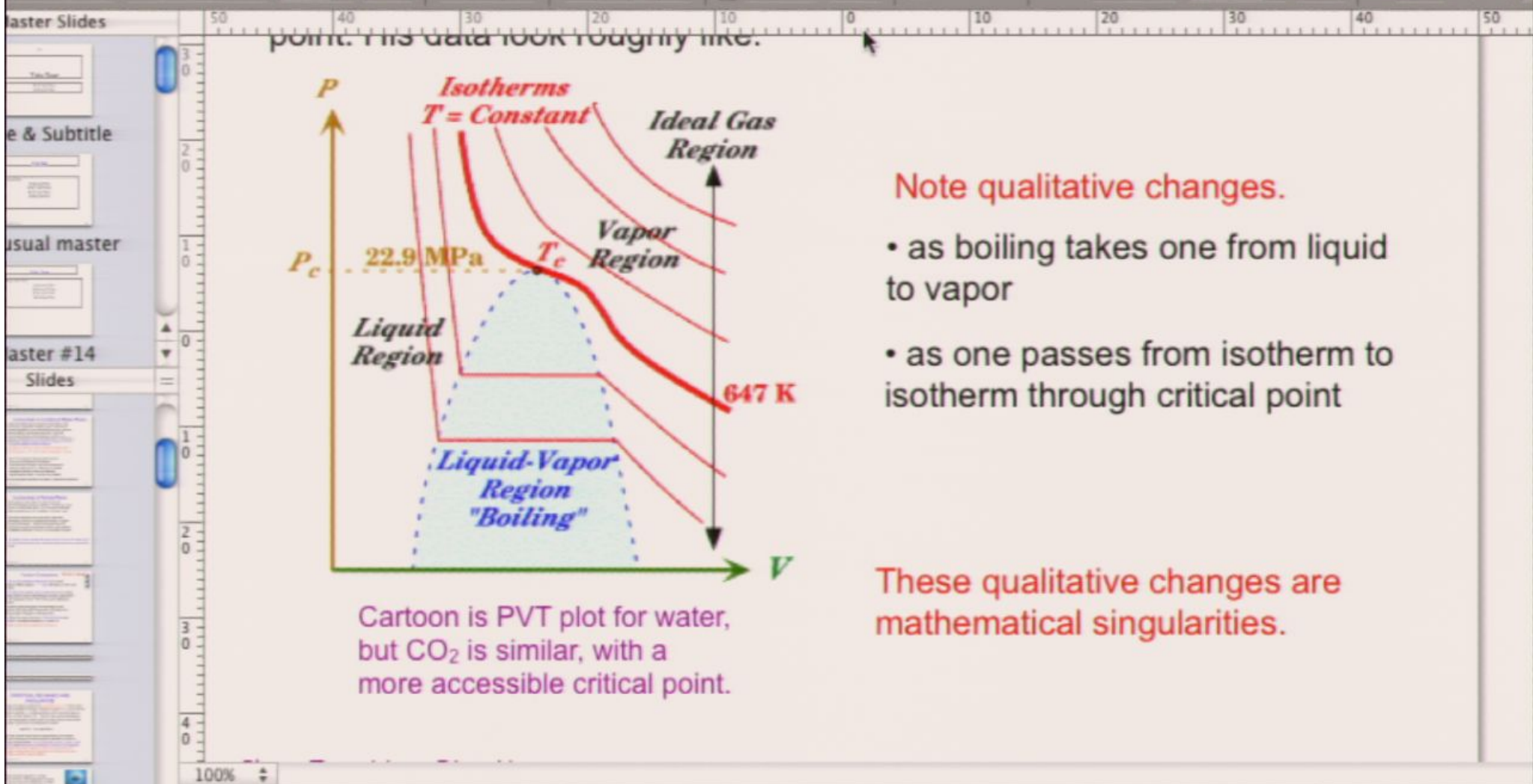
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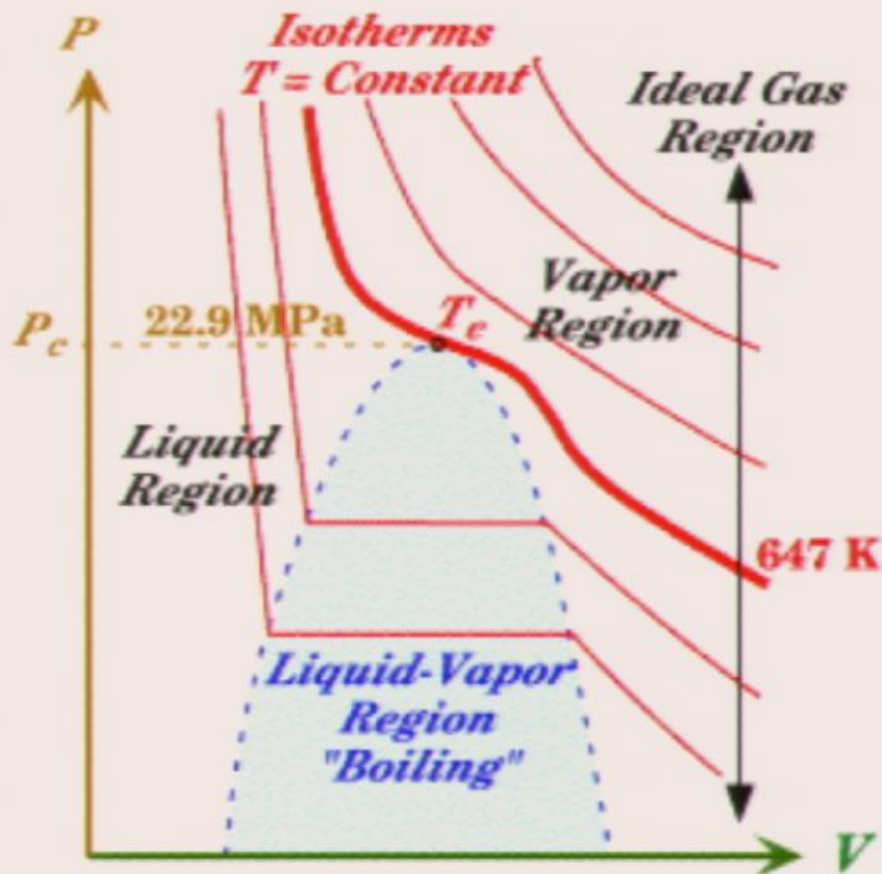
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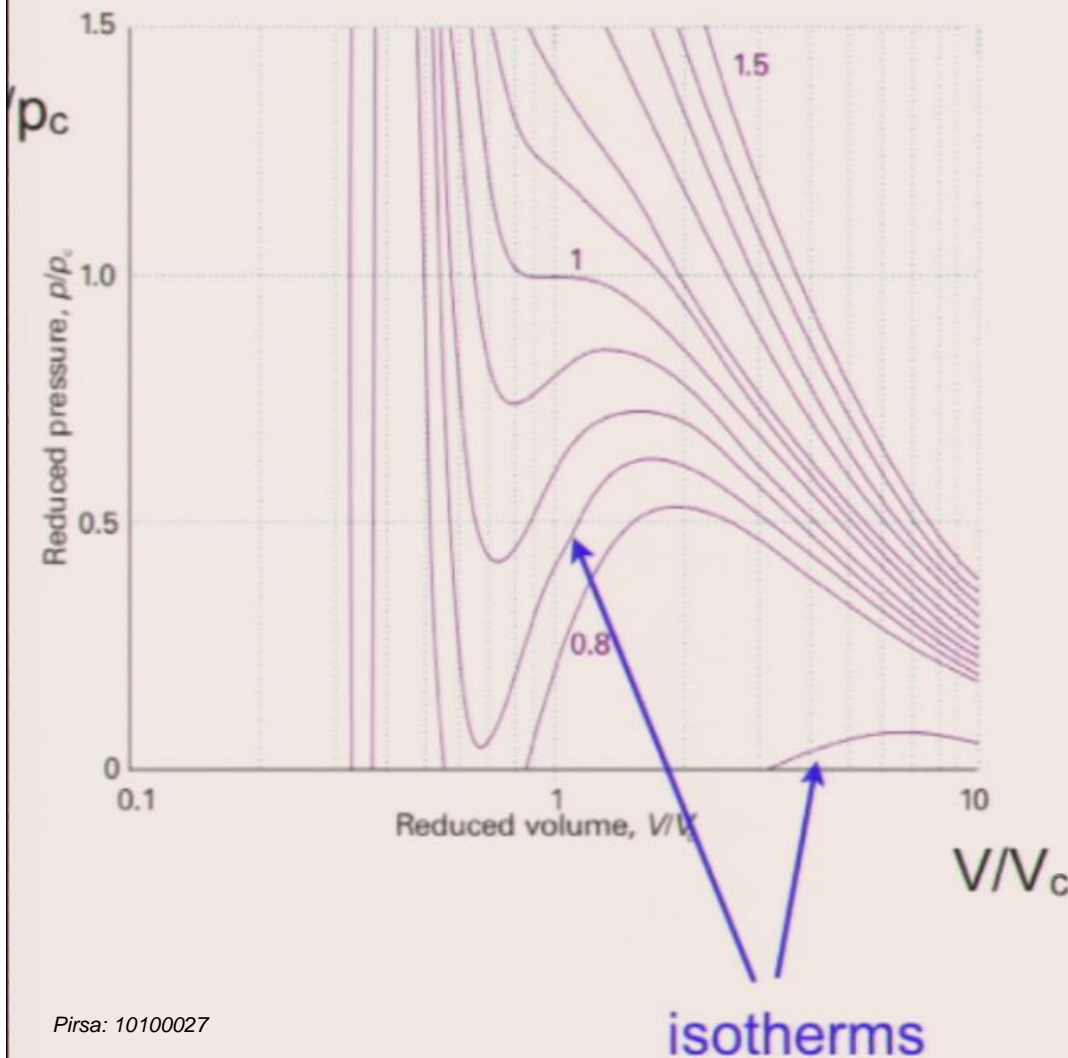
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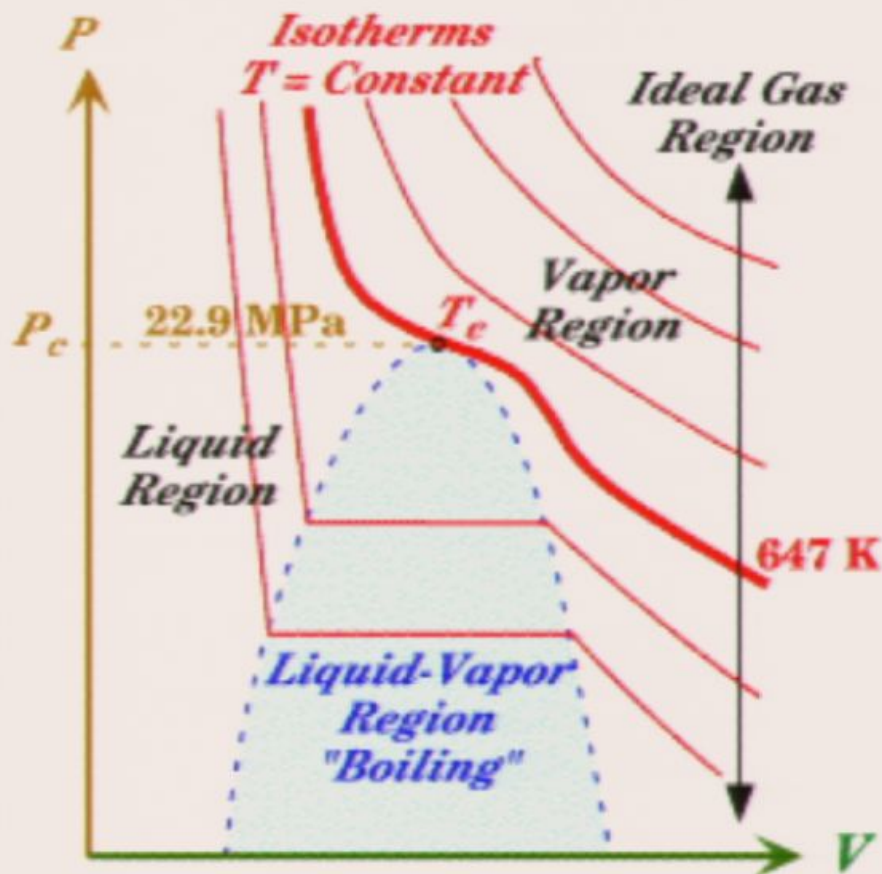
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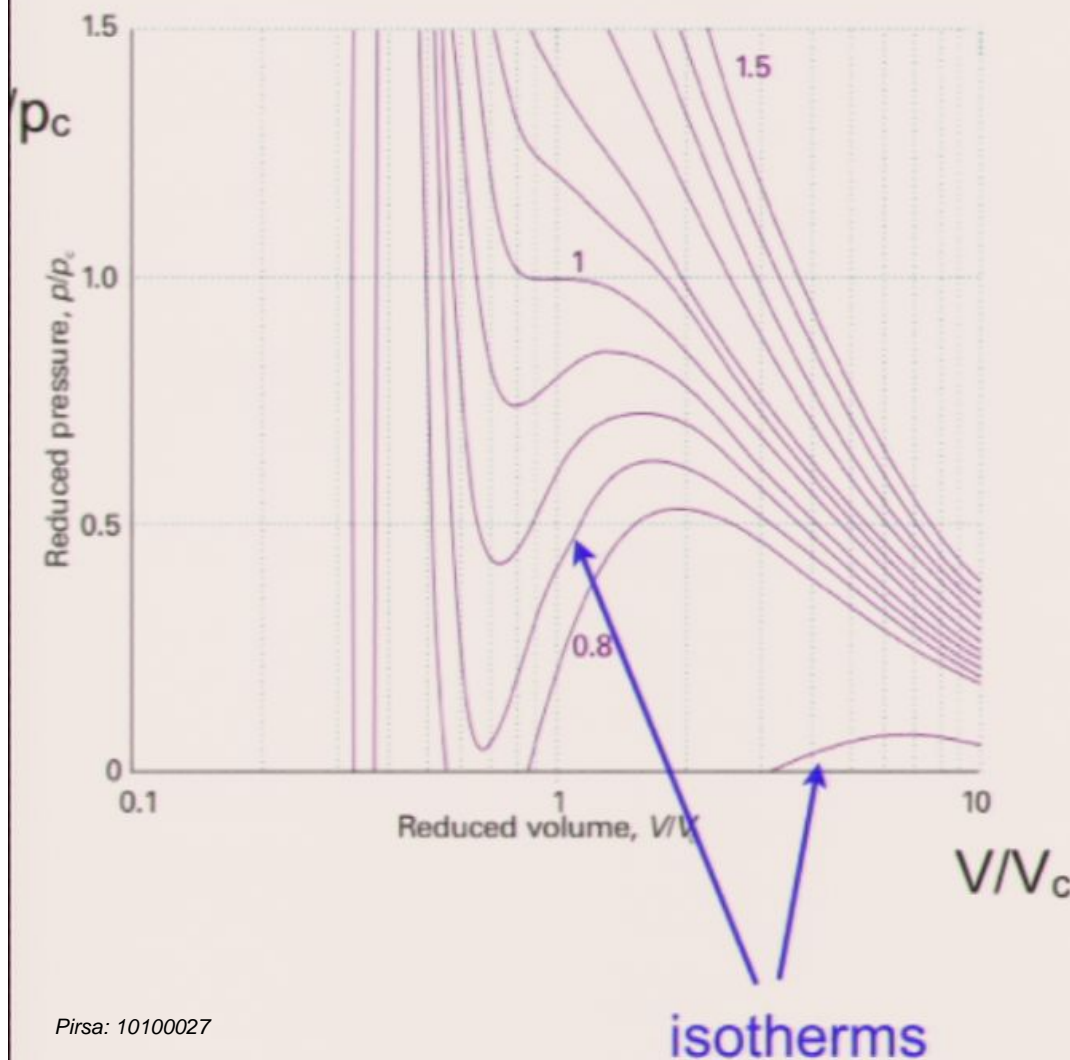
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evidence
for Atoms

Molecules?

$$pV = NkT \text{ Plank stat mech}$$

$$N_p = \frac{1}{e^{\beta \hbar \omega_p}}$$

$$\sum_{n=0, \dots, \infty} e^{-\beta \hbar \omega_p n} = \frac{1}{1 - e^{-\beta \hbar \omega_p}}$$

closed
14 N_p

$pV = NkT$ | Plank | stat mech

$$N_p = \frac{1}{e^{\beta \hbar \omega_p}}$$

$\sum_{n=0, \dots, \infty} e^{-\beta \hbar \omega_p n}$
 $\frac{1}{1 - e^{-\beta \hbar \omega_p}}$
 $1 + N_p$
 closed

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derives an approximate
equation of state for fluids:

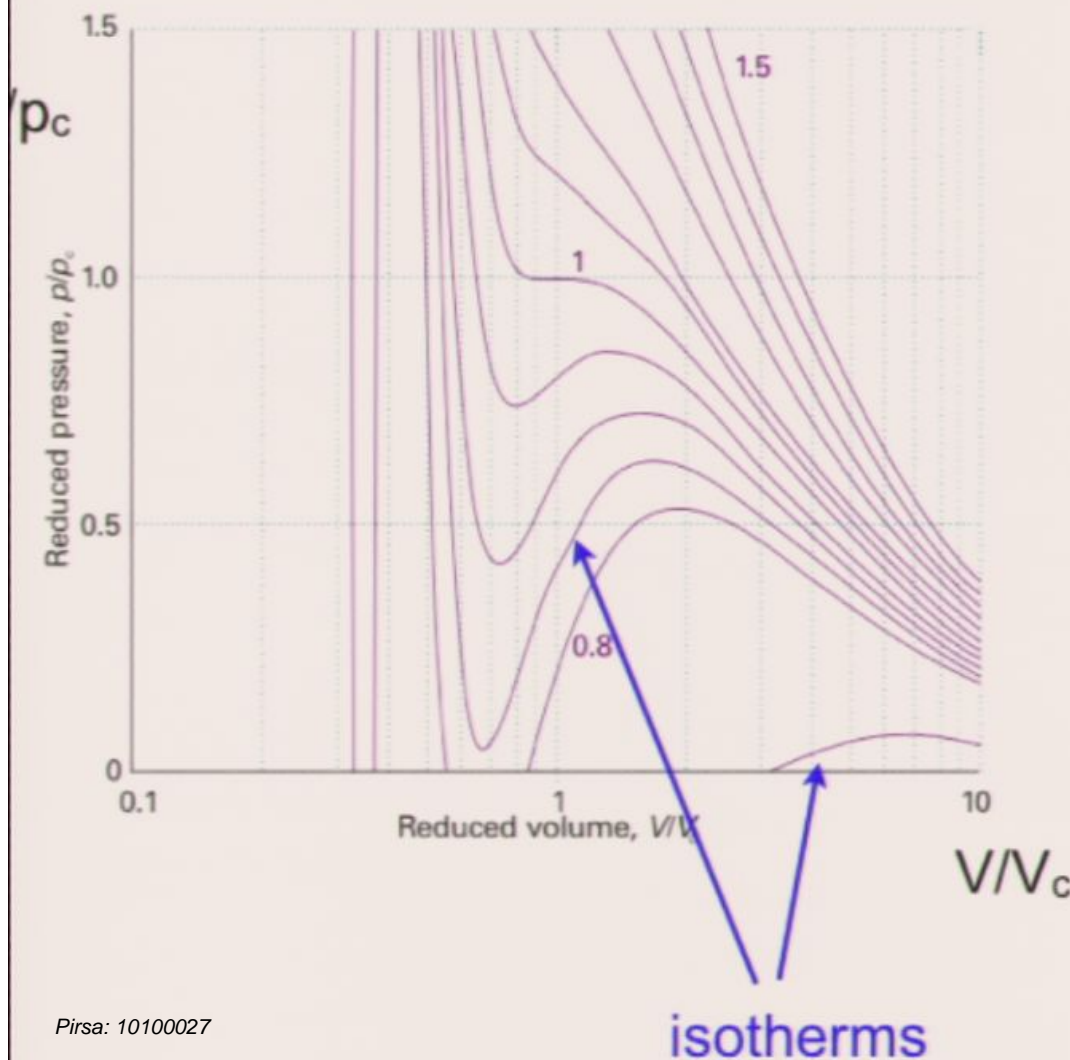
Starts from $pV=NkT$, he gets
cubic equation

$$(p + aN^2/V^2)(V - Nb) = NkT$$

Takes into account

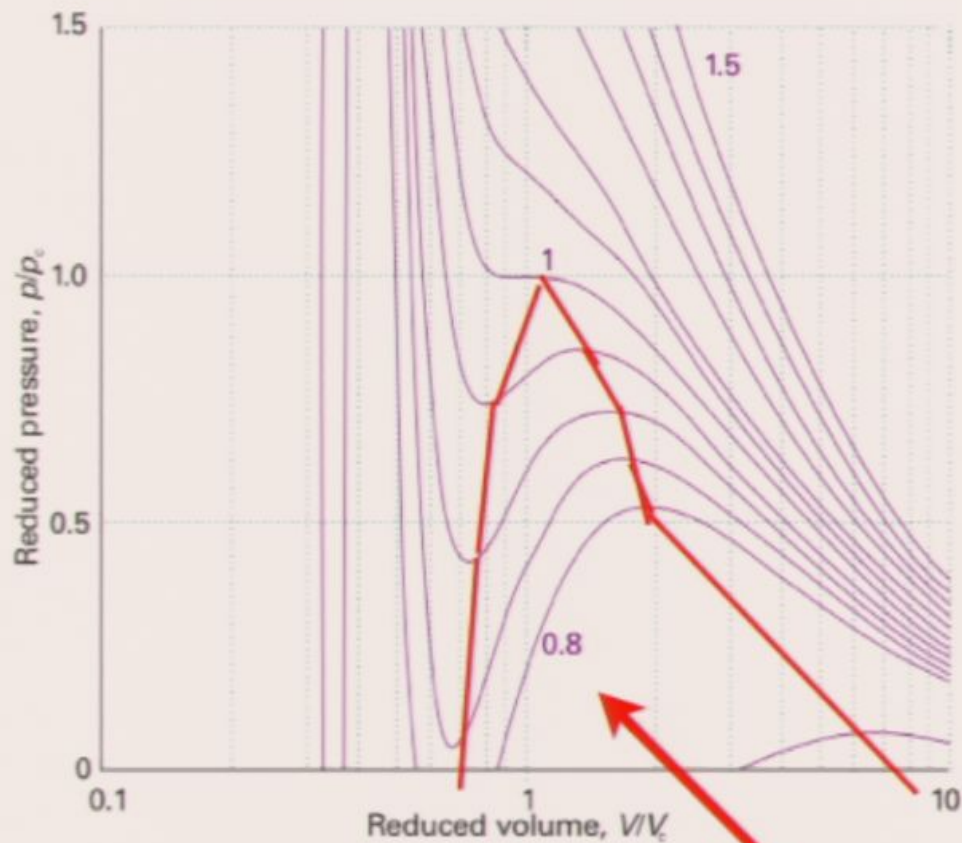
- **strong repulsive interaction** via excluded volume (bN), and also
- **attractive interactions** via potential of mean force (aN^2/V^2), (accurate for long-ranged forces.)

This work gives the first
example of a **mean field theory**
(MFT).



Note that there is here no
reference to infinite size of
system, no singularities and no
phase transitions

But **van der Waals'** result is
not entirely stable.

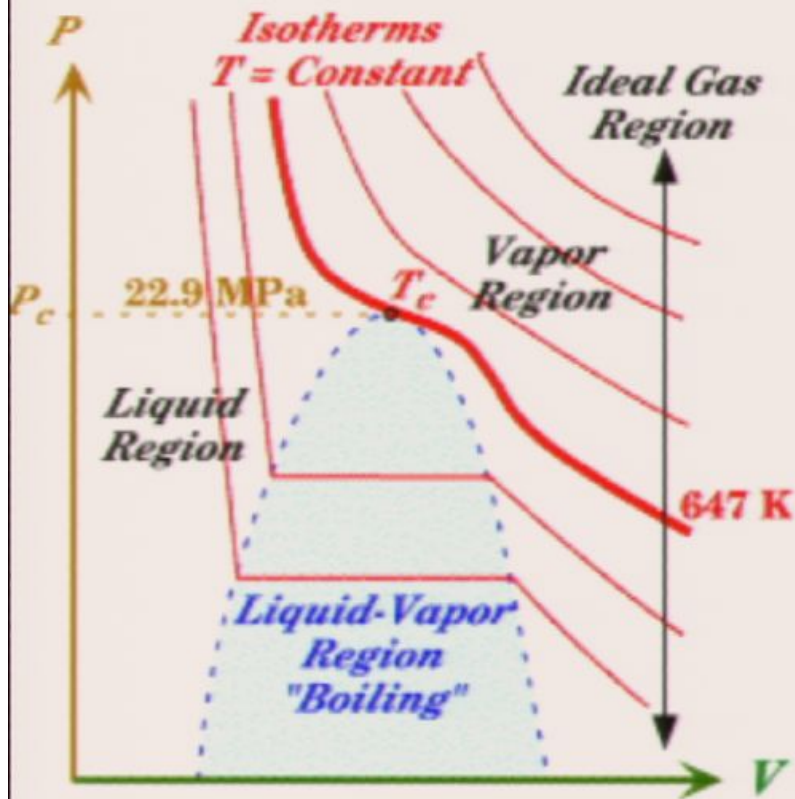


Red delimits region of absolute (mechanical) instability,
where theory must be wrong

(1875) Maxwell fixes up phase diagram

he puts in density jumps
required by thermodynamics

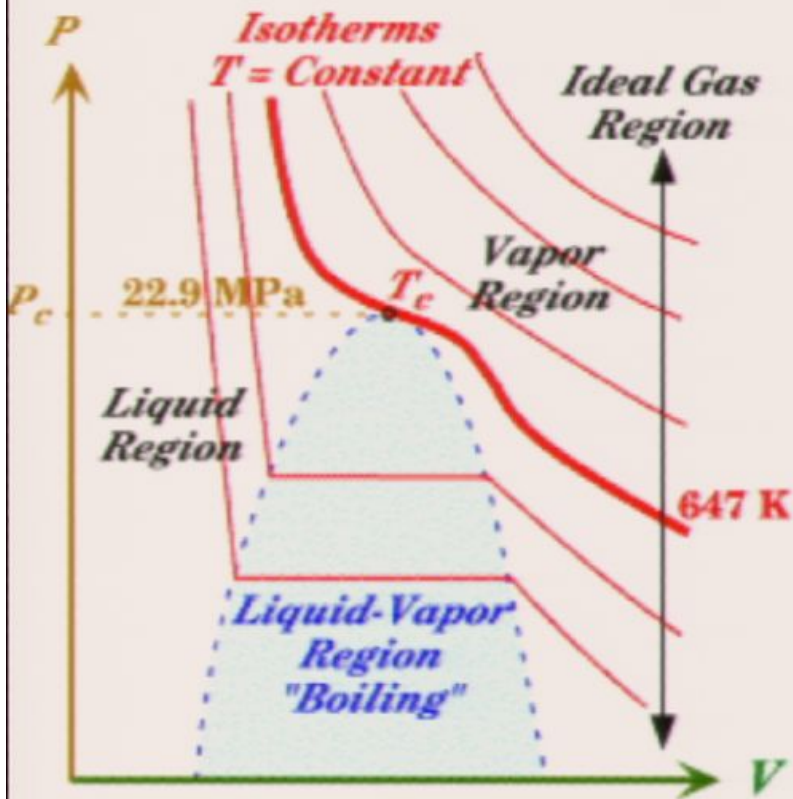
J.C. Maxwell *Nature*, **10**
407 (1874), **11** 418 (1875).



Cartoon P-V diagram for water
but CO_2 is quite similar.

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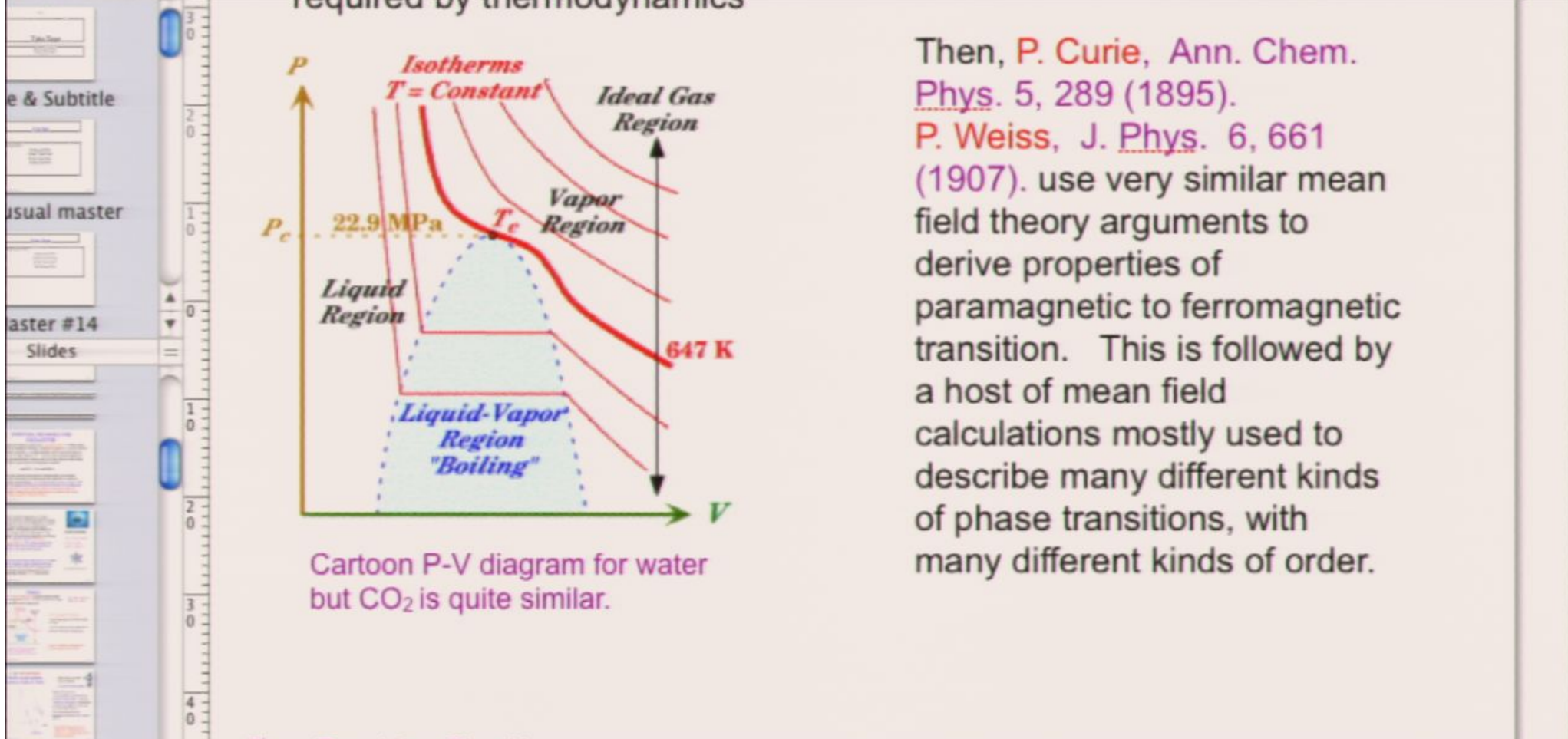
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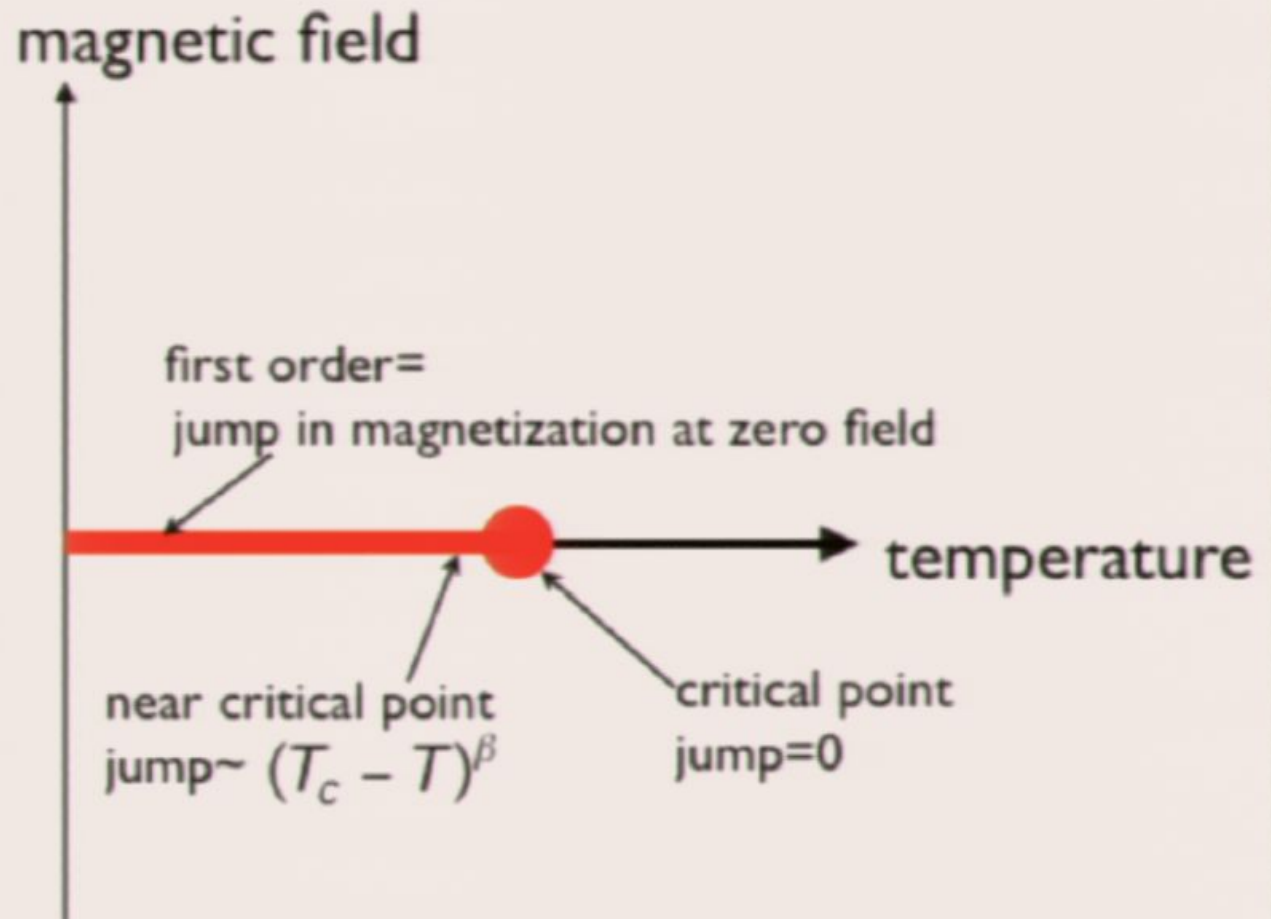


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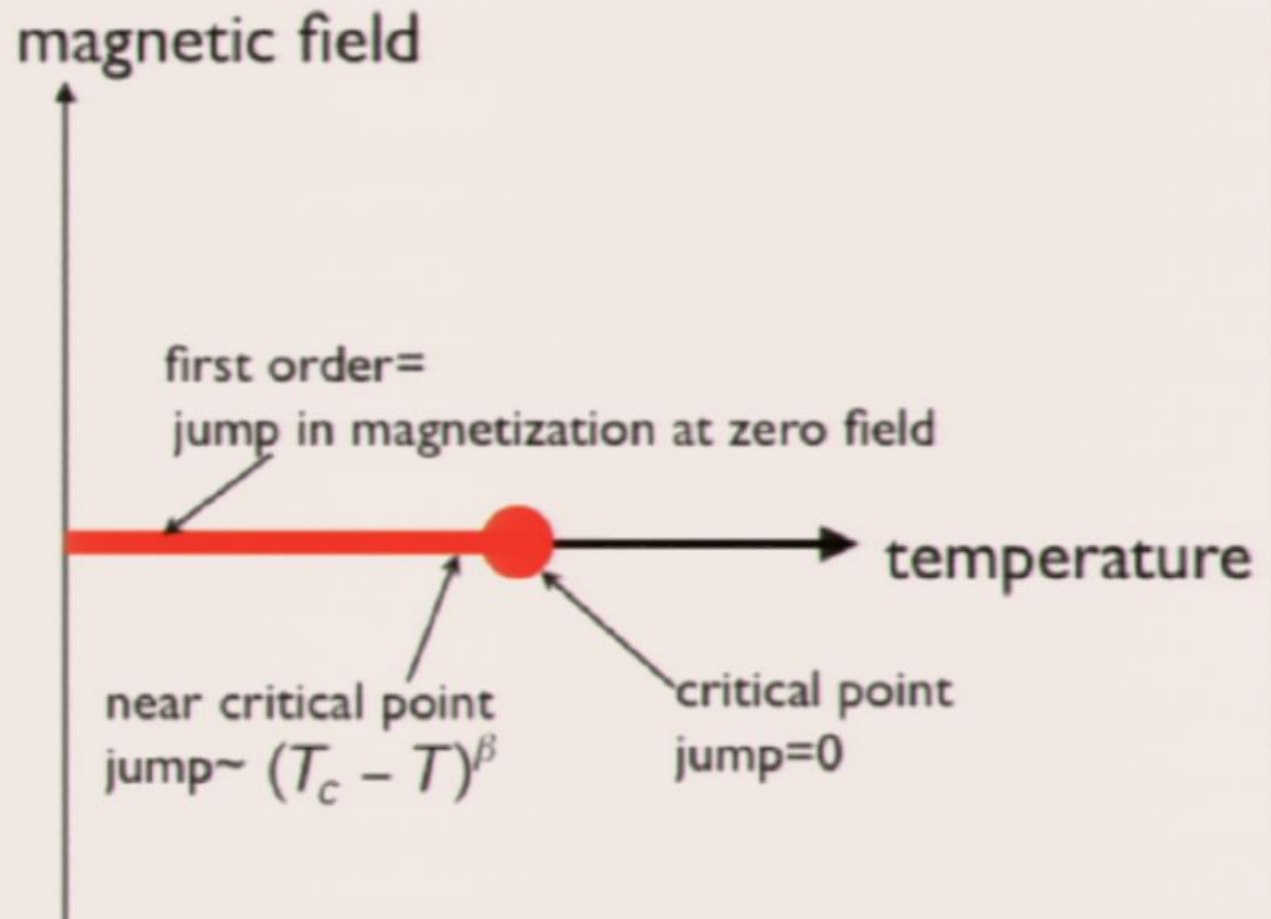
Magnetic Phase Diagram

Conceptually, the simplest phase transitions occur in ferromagnetic materials in which neighboring spins tend to align in the same direction making a magnetic field in that direction. Below a critical temperature, T_c , this alignment can occur even in the absence of an applied magnetic field.



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easiest problem: Ising ferromagnet spin, σ_r at each site of lattice, each spin takes on values plus or minus one.

problem
defined by

$$-H/(kT) = K \sum_{nn} \sigma_r \sigma_s + h \sum_r \sigma_r$$

free energy
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$$-F/(kT) = \ln \sum_{\{\sigma_r = \pm 1\}} \exp[-H\{\sigma_r\}/(kT)]$$

$\langle \sigma \rangle$ depends on K and h . Even when $h=0$, if $K>0$ spins line up and $\langle \sigma \rangle$ chooses to be non-zero.

Focus on Ising model to see nature of MFT's.

in MFT more is the same

one spin

statistical average: $\langle \sigma \rangle = \tanh h$

many spins

focus on one spin

$$-H_{\text{eff}} / (kT) = \sigma_r [h_r + K \sum_s \langle \sigma_s \rangle]$$

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$$h_{\text{eff}} = [h + Kz \langle \sigma \rangle] \quad z = \text{number of nn}$$

$$\langle \sigma \rangle = \tanh(h_{\text{eff}})$$

or, if there is space variation, $h_{\text{eff}} = h_r + K \sum_{s \text{ nn to } r} \langle \sigma_s \rangle$

We shall focus on these equations for a time. This is an approximation called MFT. We would like to understand the qualitative structure of the phase diagram for the Ising model by looking at the MFT results.

Look near saturation for positive K

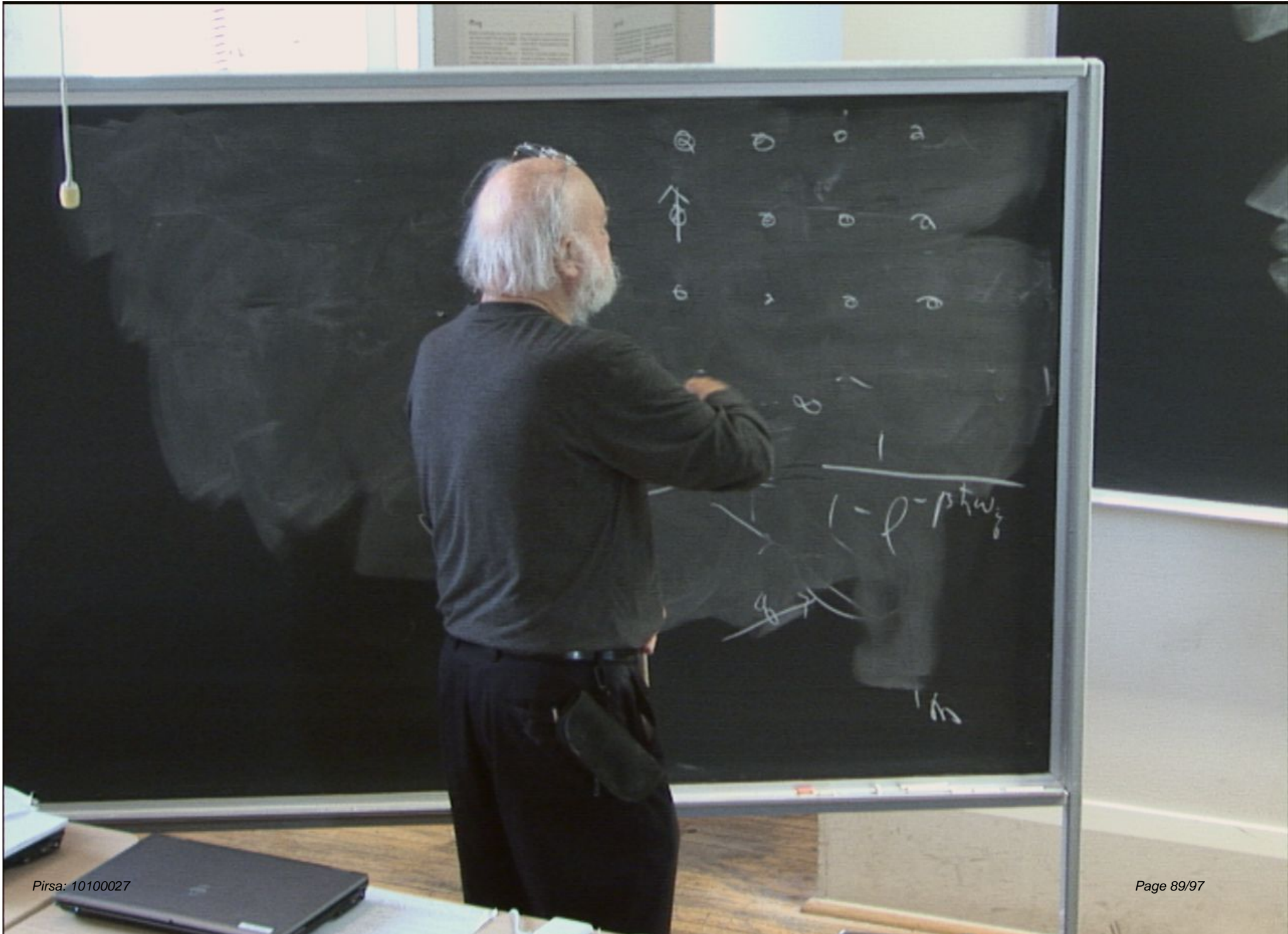
The maximum possible value of $\langle \sigma \rangle$ is 1 and that happens when K is large or when h is a large positive number, so h_{eff} is large too

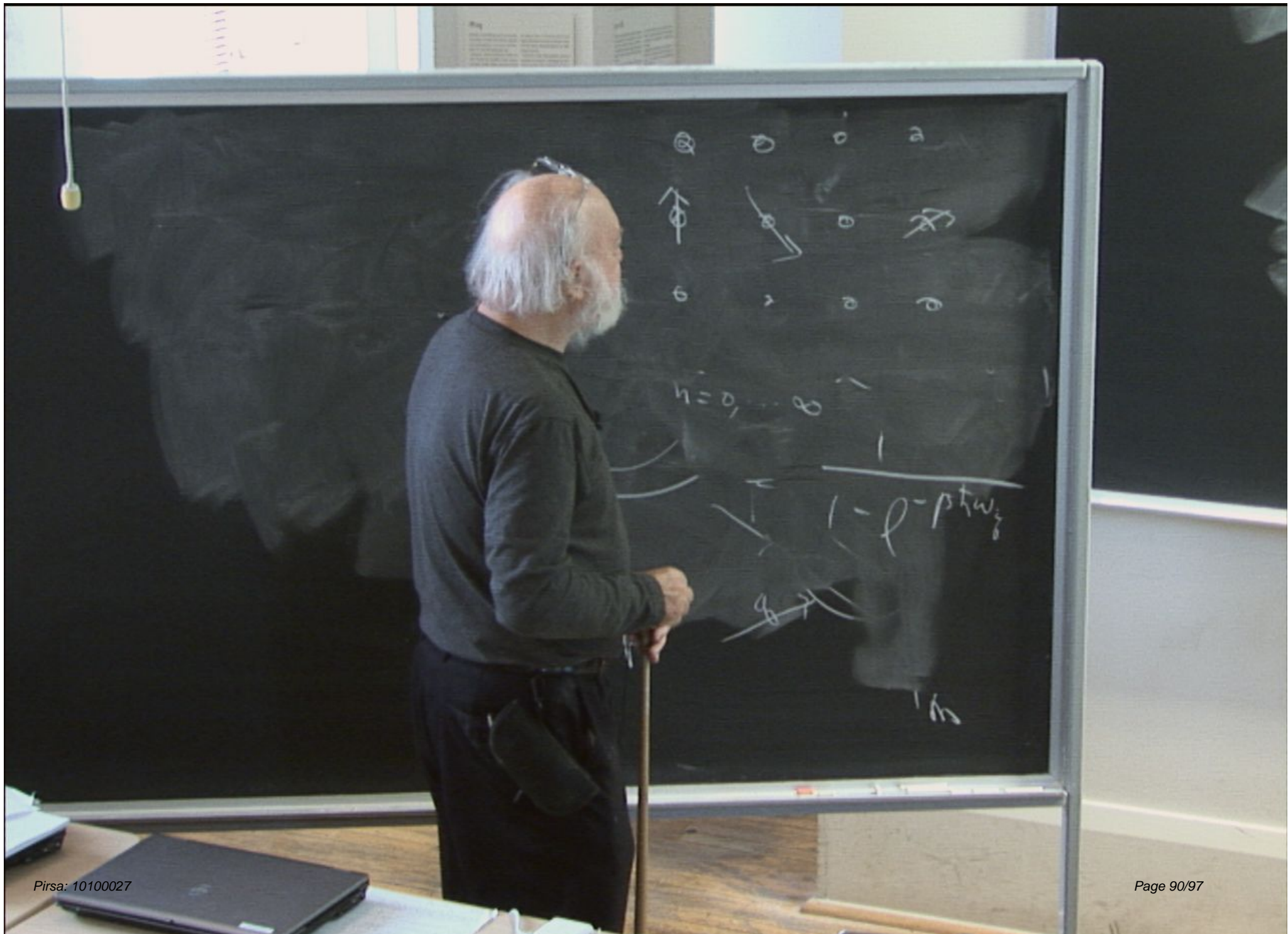
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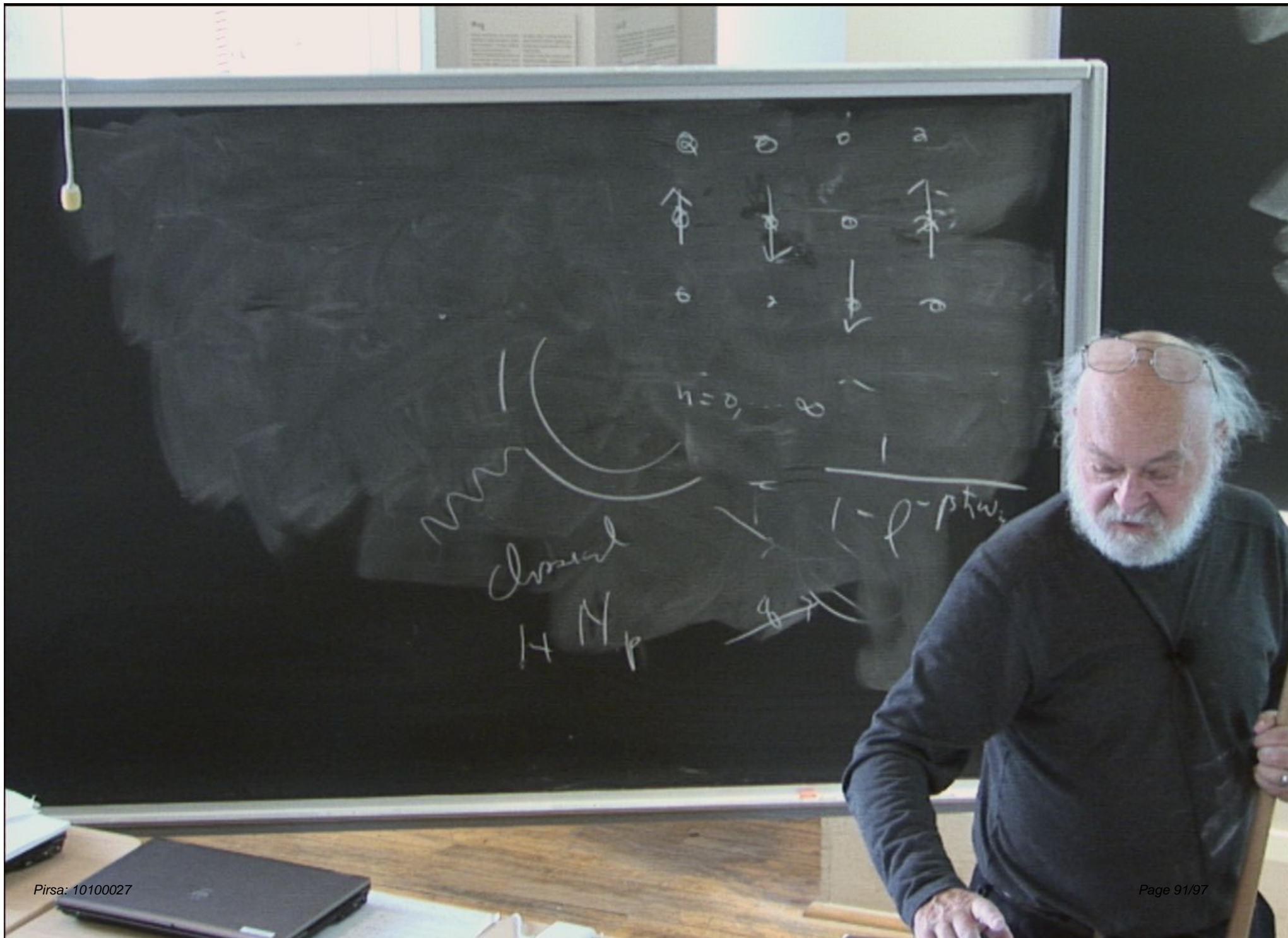
lowest order: $h_{\text{eff}} = h + Kz$ large and positive
 $\langle \sigma \rangle = 1 - 2 \exp[-2h_{\text{eff}}]$

with large K and negative h we also have the flipped solution
 $\langle \sigma \rangle = -1 + 2 \exp[2h_{\text{eff}}]$ $-h_{\text{eff}} = -h + Kz$ large and positive

Thus there are two different solutions with almost saturated values of $\langle \sigma \rangle$ which both arise for large K. The stable solution has the lowest free energy, and a little analysis shows that this lowest solution has $\langle \sigma \rangle$ with the same sign as h. Therefore $\langle \sigma \rangle$ can jump when the sign of h changes.







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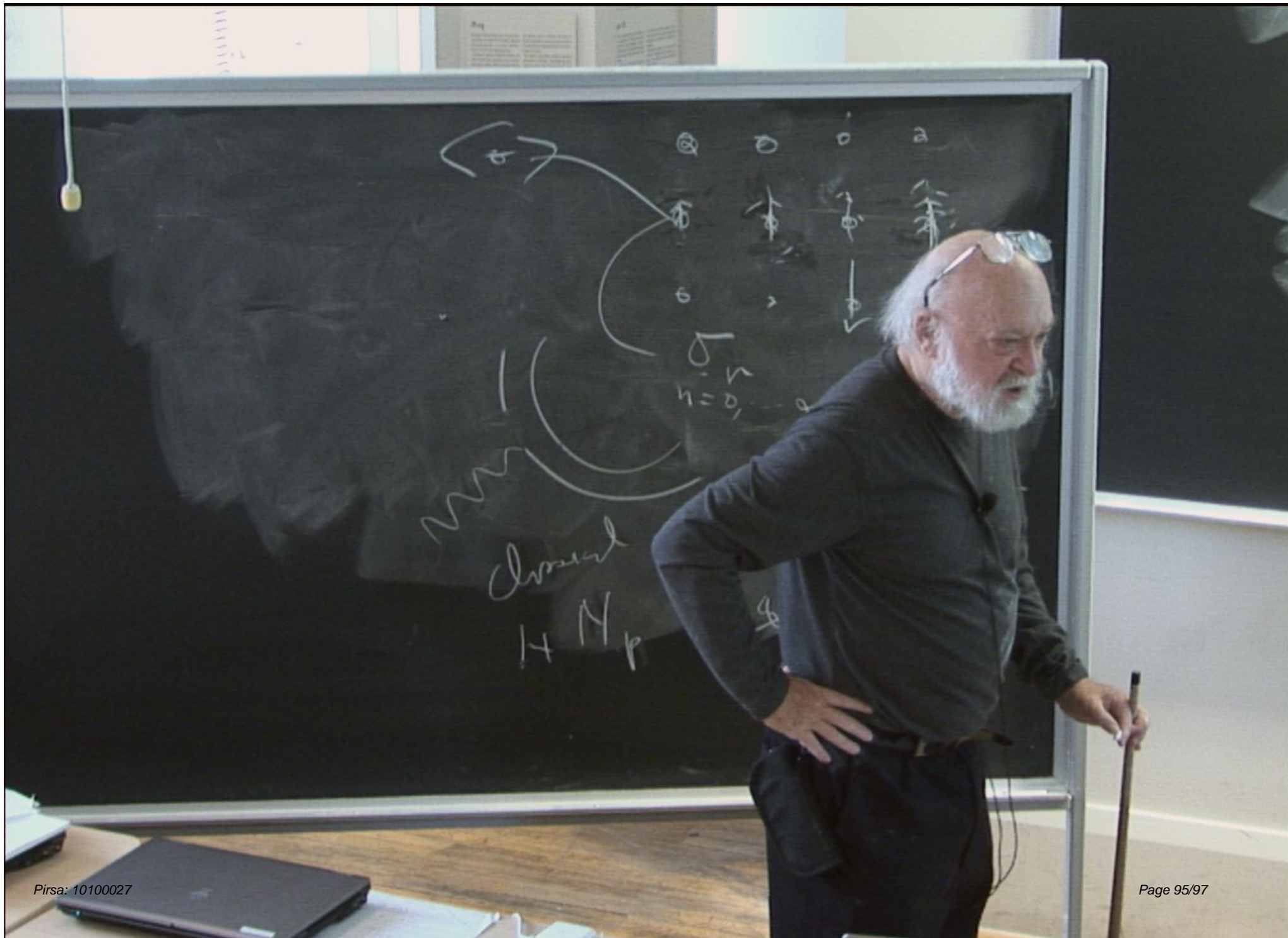
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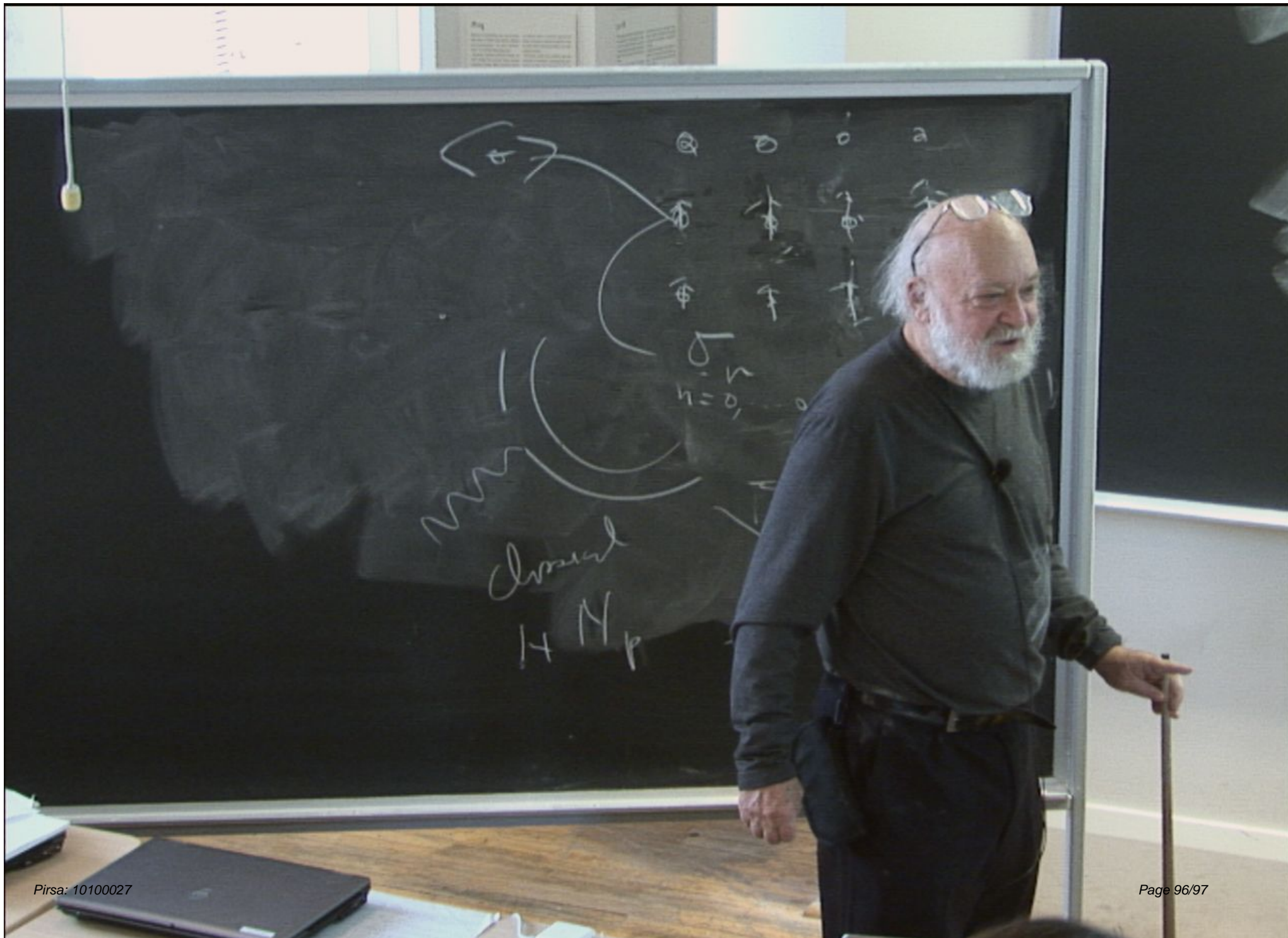
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