

Title: Statistical Mechanics (PHYS 602) - Lecture 10

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Abstract:



Order Parameter, generalized

One very important moment occurred in 1937, when Landau pointed out the basic unity among all the different MFT's.

- **Lev Landau** suggested that phase transitions were manifestations of a broken symmetry, and used the order parameter to measure the extent of breaking of the symmetry.
- in ferromagnet, parameter = magnetization
- in fluid, order parameter = density
- in Ising model, order parameter = $\langle \sigma \rangle$



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L.D. Landau

Start here

I'm going to talk about considerable history of science in this lecture. I'll focus for a bit on the year 1937.

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Generalized Mean Field Schemes I

Landau generalized the many different MFT's that existed by assuming an expansion of the free energy in an order parameter, here symbolized by M = magnetization

$$F = \int dr [a - hM + tM^2 + cM^4 + (\nabla M)^2]$$

expansion assumes a small order parameter (works near critical point) and small fluctuations (works far away?!)

h is magnetic field

t is proportional to $(T - T_c)$

minimize F in M : result General Solution $M(h, (T - T_c))$

singularity as t, h both go through zero!

singularity as h goes through zero for $T < T_c$

note: no cubic term
This free energy applies to symmetry breaking models

Vary $M(r)$ to vary F

$$F = \int dr [a - hM + tM^2 + cM^4 + (\nabla M)^2]$$

Integrate by parts in gradient term

$$\delta F = \int dr \delta M(r) [-h + 2tM(r) + 4cM(r)^3 - \nabla^2 M(r)]$$

to minimize F , coefficient of $\delta M(r)$ must vanish

$$0 = -h + 2tM(r) + 4cM(r)^3 - \nabla^2 M(r)$$

Hence we have an equation for M ! That is a general equation for the order parameter in mean field theory with the **Z2 symmetry**, i.e. symmetry under sign change of M .

Our result is exactly the same cubic equation as the equation we derived for the MFT of the Ising model, so we need not do much further analysis. (We also saw this in the van der Waals equation.)

Note that the theory includes F , so when there are several solutions, we can pick the right one.

Why minimize?

Thermodynamics says that the free energy is extremized by the variation in any macroscopic parameter, e.g. any extensive variable. This is part of a general idea that the free energy is a probability, which arises from how the partition function is used. In statistical mechanics only the most probable things happen. This applies to all macroscopic phenomena, Now $M(r)$ is not quite macroscopic, but Landau's idea was that at the long wavelength part of it it was "macroscopic enough" so that one could neglect its fluctuations. This point of view has turned out to be wildly successful.

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This same approach is still in extensive use.

$$= \mathcal{F}_n + \int d\mathbf{r} \left\{ \frac{1}{2m} |\nabla \Psi(\mathbf{r})|^2 + \alpha(T) |\Psi(\mathbf{r})|^2 + U(\mathbf{r}) |\Psi(\mathbf{r})|^2 + \frac{b}{2} |\Psi(\mathbf{r})|^4 \right\}$$

Superfluid density near the critical temperature in the presence of random planar defects

D. Dalidovich, A.J. Berlinsky and C. Kallin

*Department of Physics and Astronomy, McMaster University,
Hamilton, Ontario, Canada L8S 4M1*

(Dated: November 14, 2008)

order parameter and free energy were crucial concepts used by Landau

free energy could be expressed in terms on any descriptors of systems behavior. It is a minimized by the correct value of any one of them, We have thus come loose from the particular thermodynamic variables handed to us by our forefathers,

order parameter could be anything which might jump in the transition.

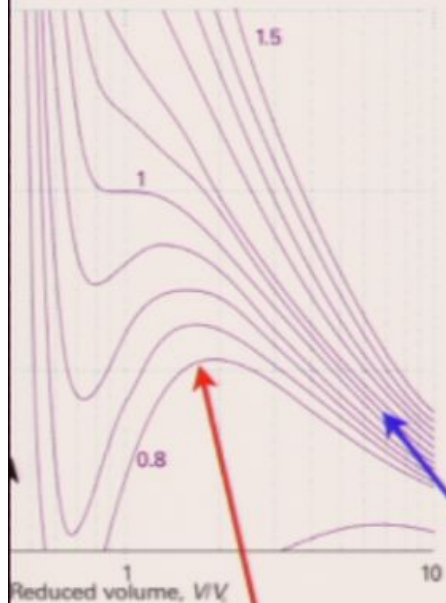
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A little later, Julian Schwinger was working on electromagnetic fields for World War II radar. He use variational methods and effective fields (“lumped variables”) to build electromagnetic circuits. Together Landau and Schwinger convinced people that variation methods could be very useful.

In that same 1937 at a statistical mechanics conference in
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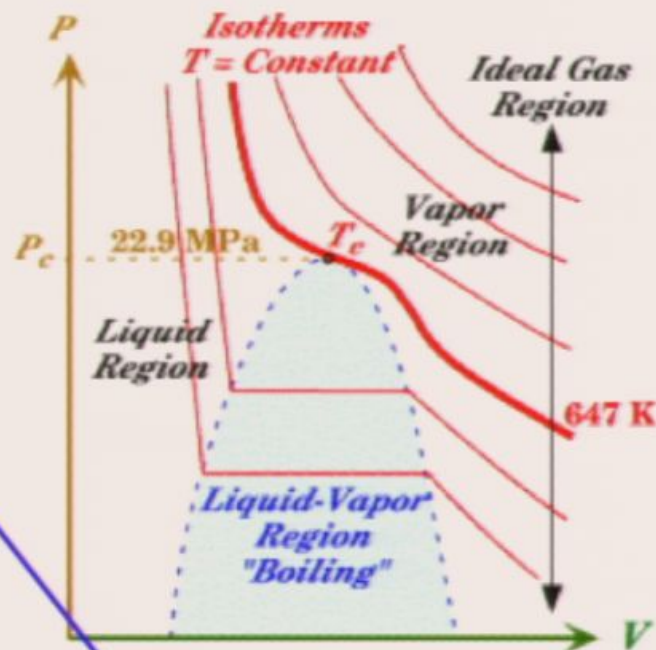
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stat mech theory
van der Waals



mixed state
region:
instabilities

Maxwell &
experiment



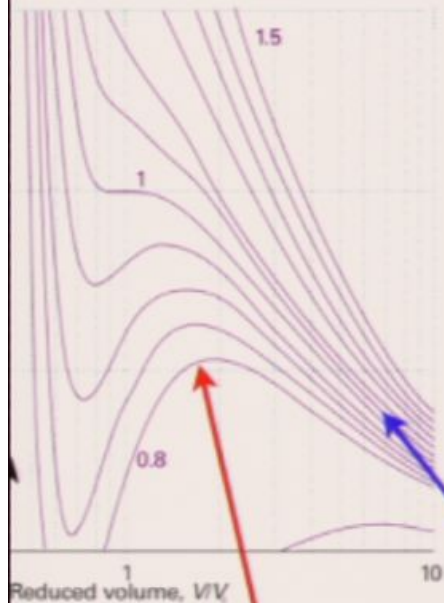
vapor region:
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Kramers* chairs a session. He knows extended singularity theorem, i.e. that for finite N picture on the right (**with singularities!**) is incompatible with statistical mechanics of finite system. Picture on left is incompatible with thermodynamics.

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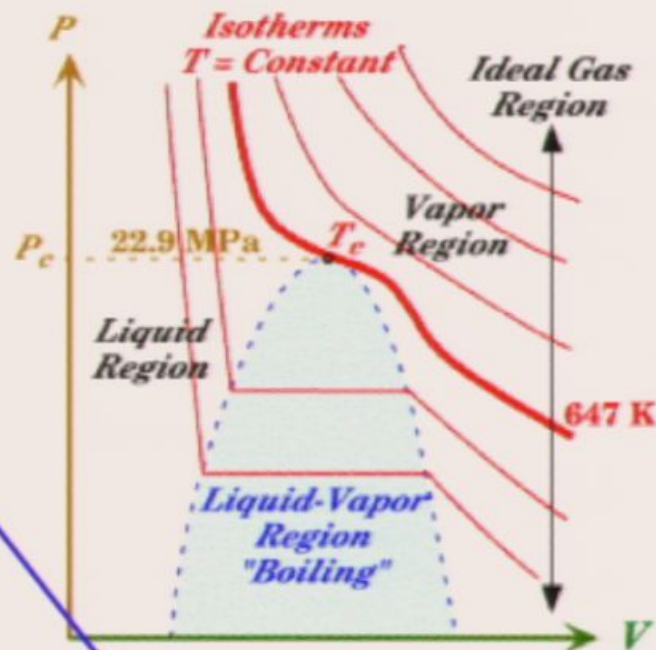
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Conference is perplexed. It votes on proposition of whether statistical mechanics can describe liquid region. Outcome: 50-50 with Debye!! voting "nay".

This is **wrong answer, liquids are described by statistical**

Arthur Wightman on this history*:

“There is one aspect of the thermodynamic limit that Gibbs does not emphasize. That is the appearance of phase transitions between distinct thermodynamic phases..... [S]harp phase transitions do not occur in finite systems. A little more pedagogical zeal by Gibbs could have saved some of the generations that followed considerable time....Gibbs could have told them that it was pointless to discuss [phase transitions] except in the thermodynamic limit.”

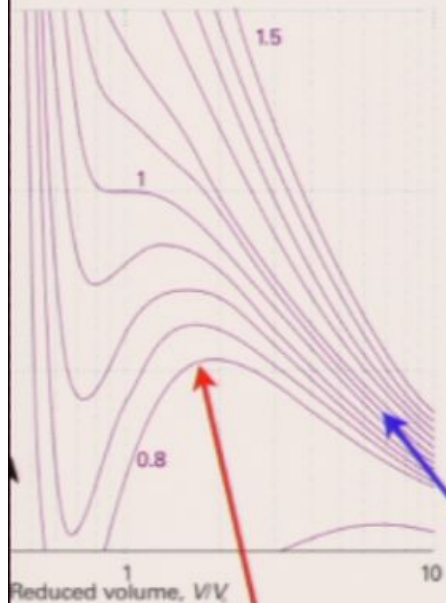
For myself, I don't think that Gibbs fully understood the way that the thermodynamic limit works for phase transitions.

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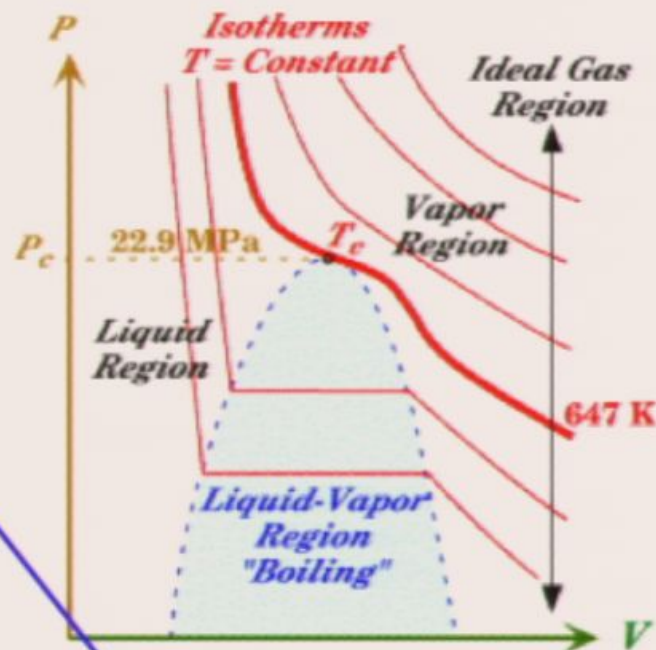
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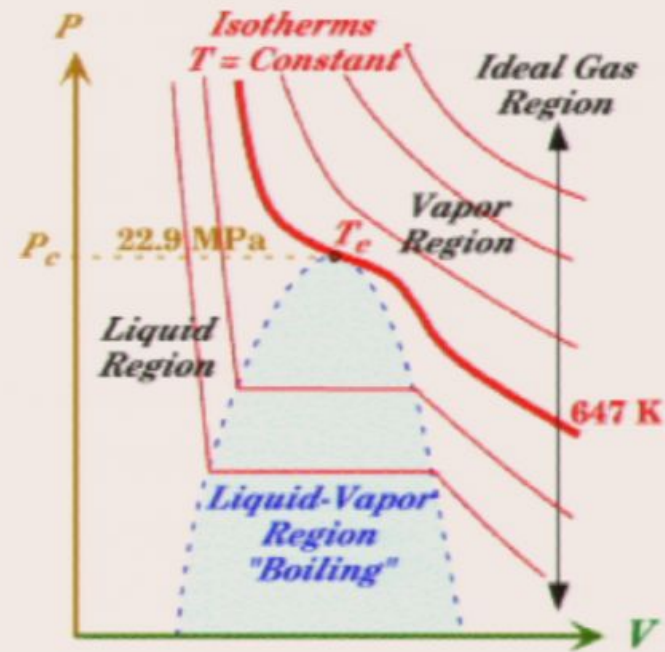
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Application to Phase Transitions: today's view

- thermodynamic phase transitions involve singularities, and infinities arising (almost always) from unbounded numbers of particles
- these infinities appear in thermodynamic derivatives which is caused by a coherence length (correlation length) that diverges*
- in practice coherence length describes spatial extent of fluctuations that look like regions of two phases intermixed, e.g. drops of vapor in liquid or drops of liquid in vapor.



statistical mechanics does mostly fail, but not in liquid region--- rather in boiling region.

The approximate theories of stat mech (e.g. MFT's) must be improved near critical point.

theories available in 1937 all fail near

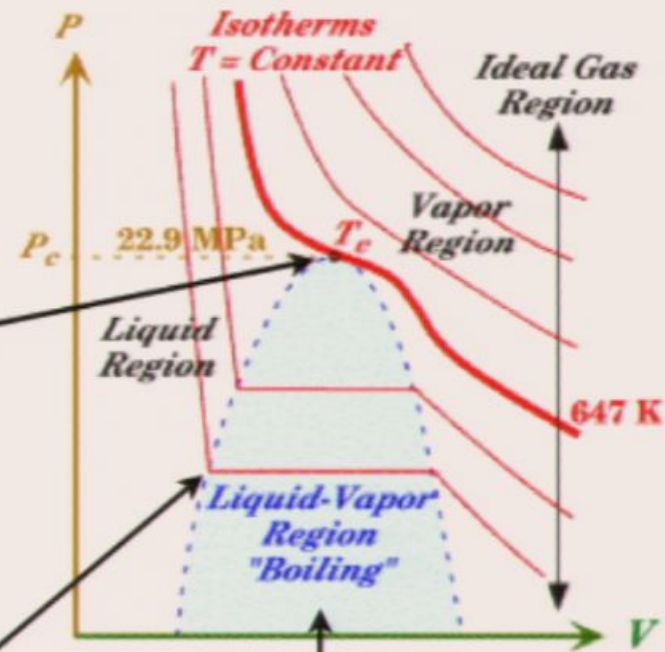
* This divergence makes extended similarity theorem work

Application to Phase Transitions: today's view..., continued

finite size of real systems cuts off infinities, for example, in the derivative of density with respect to pressure, at some very large value.

finite size of real systems produces small regions of rounding here rather than sharp corners

statistical mechanics mostly fails in boiling region.



I call this result, that phase transitions need an infinite system the **extended singularity theorem**

extended, because the anomalous thermodynamic behavior is caused by the whole infinite system,

singularity, because the anomalous behavior is a singularity

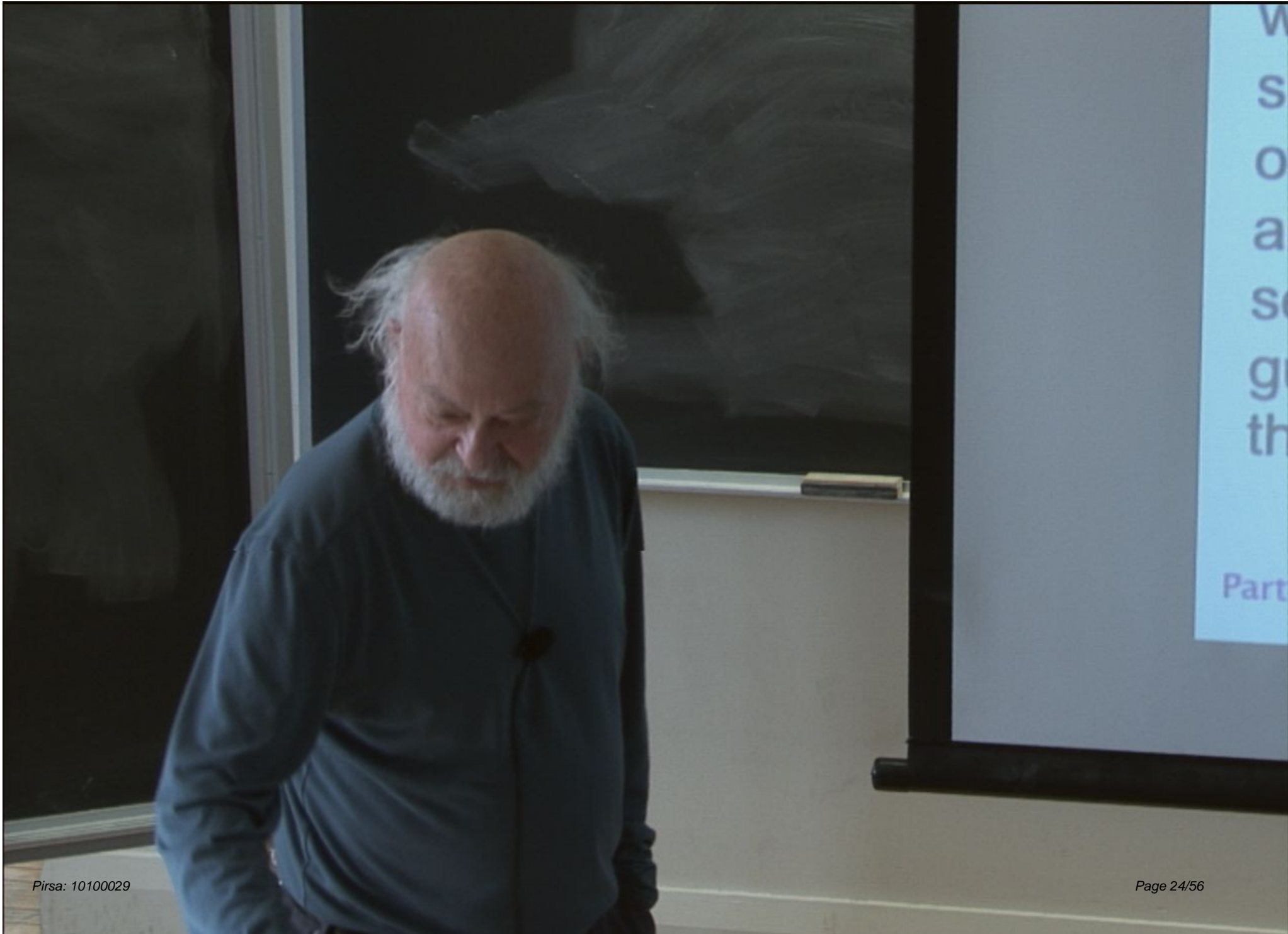
theorem, because this is a mathematically rigorous result

logically, this result should have pointed to a major difficulty of mean field theory, and should have pointed people away from MFT. After all, MFT did not include any hint of spatial infinity, nor of any part of the extended singularity theorem. But mean field theory had in it, one final triumph: the theory of superfluidity.

Sound

Superconductivity remained mysterious for many years. Obviously it was connected with infinite conductivity. Then Meissner effect ([Walther Meissner](#) and [Robert Ochsenfeld](#) 1933) showed that magnetic field was expelled from inside of a conductor.

Superfluidity was almost equally mysterious. Einstein had suggested that a Bose system could enter into a state in which a finite fraction of the molecules would end up in a single quantum state. However, Uhlenbeck talked him out of thinking that this would produced a phase transition and an explanation for superfluidity, because Uhlenbeck could see that no such transition would occur in a finite system. I guess Uhlenbeck did not understand extended singularity theorem.



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Yee Lee

$$\frac{\hbar}{i} \partial_t \psi(r,t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(r,t) + \int d\mathbf{r}' V(\mathbf{r}-\mathbf{r}') \psi(\mathbf{r}',t)$$

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$$\psi(r,t) = \langle \psi(r,t) \rangle + \delta \psi(r,t)$$

John Bardeen did his BCS work at the age
of 49

deemphasized the connection between BCS and
superfluidity
superfluidity treated by Bogoliubov
then Blatt, Butler, Schfroth.



a fine gentleman.

He gained a Nobel prize for his work, joint with Brattain
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BCS Theory

BCS put together a most impressive theory of superconductivity. Bardeen was the impresario and leader. He had questions he wanted answered about superconductivity and made sure the joint work answered everything he could think of about the subject.

Leon Cooper, a postdoc, did a theory of pairing of electrons based upon an attractive interaction between electrons produced by the frequency dependent electron phonon interaction.

Bob Schrieffer, a brilliant grad, student produced a trial wave function (based upon the previous work of Tomonaga) to be plugged into a variational principle.

Together they explained almost all the known microscopic properties of superconductors.

“Hydrodynamics” and transport in different phase of matter

Different phases of matter are qualitatively different. The only exception mentioned here is the liquid/vapor system in which both phases are qualitatively similar.

Each kind of phase has its own kind of long-wave-length or transport process. For example, a liquid has no rigidity so it cannot transfer a torque over a long distance, but a solid can. At low frequencies momentum transfer in liquids involve one kind of sound wave and two components of diffusion limited by viscosity. The latter is described by the Navier Stokes equations, extensively used in fluid research.

$$\partial_t \mathbf{v}(\mathbf{r}, t) + (\mathbf{v}(\mathbf{r}, t) \cdot \nabla) \mathbf{v}(\mathbf{r}, t) = \eta \nabla^2 \mathbf{v}(\mathbf{r}, t) + \nabla p(\mathbf{r}, t) \quad \nabla \cdot \mathbf{v}(\mathbf{r}, t) = 0$$

In contrast, solids have three modes of sound propagation: one longitudinal and two transverse. Each of these modes obeys an equation of the form

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$$\partial_t^2 \mathbf{v}(r,t) - c^2 \nabla^2 \mathbf{v}(r,t) = 0$$

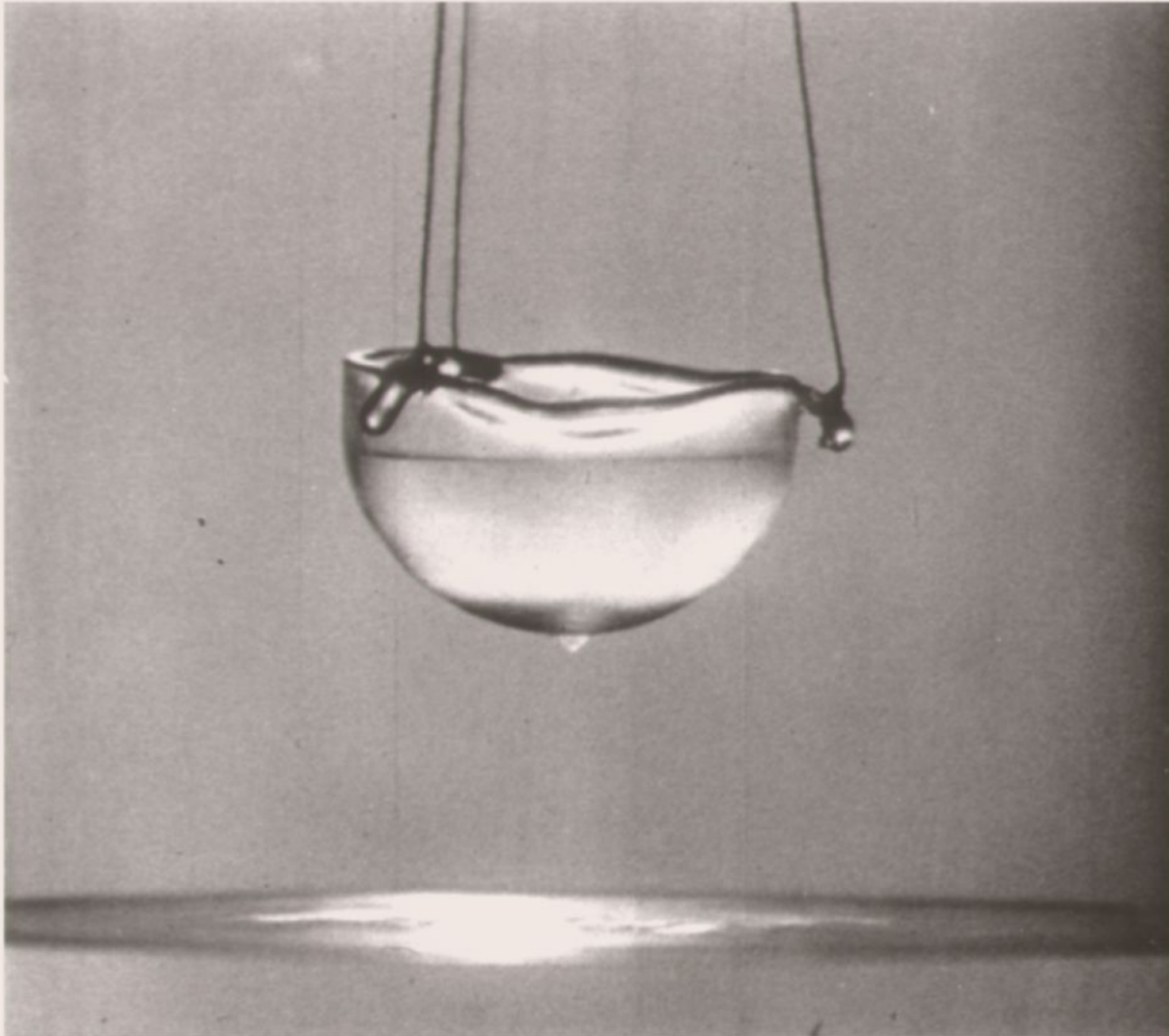
transport in different phases ...continued

Superfluids have special “super” flow processes which cannot occur in an ordinary liquid. In the simplest time-independent limit the slow changes are described by a non-linear Schrodinger equation of the form

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}^2} + V(\mathbf{r}) + \frac{4\pi\hbar^2 a_s}{m} |\psi(\mathbf{r})|^2 \right) \psi(\mathbf{r}) = \mu \psi(\mathbf{r}),$$

The right hand side comes from a term in $i (\hbar/2\pi) \partial_t \psi$, in a situation in which the energy is given by the chemical potential μ .

This is called the **Gross-Pitaevski** equation, and applies at very low temperatures. At higher temperatures, the flow equations are described as two-fluid equations, because the flow can be roughly understood as a simultaneous flow of normal fluid and superfluid. Some very special effects are produced. For example film flow.



Superconductors

An analogous situation holds in the normal low-temperature superconductors of the sort described by BCS. These have the usual solid transport processes, produced by the superconducting quasi-particles and in addition an equation for the condensate, called the Landau-Ginzburg equation. The latter is a form of Landau's equation for a critical system, with a complex wave function representing the behavior of the order parameter. Their equations take the form

$$\alpha\psi + \beta|\psi|^2\psi + \frac{1}{2m}(-i\hbar\nabla - 2e\mathbf{A})^2\psi = 0$$
$$\mathbf{j} = \frac{2e}{m}\text{Re}\{\psi^*(-i\hbar\nabla - 2e\mathbf{A})\psi\}$$

where \mathbf{j} is the electrical current produced by the superflow. Note the $2e$. That's because the wave function describes Cooper pairs. One can include a time derivative in the first equation to describe slow temporal changes.

Brian Josephson

& Harwell

unneling

DC Josephson effect

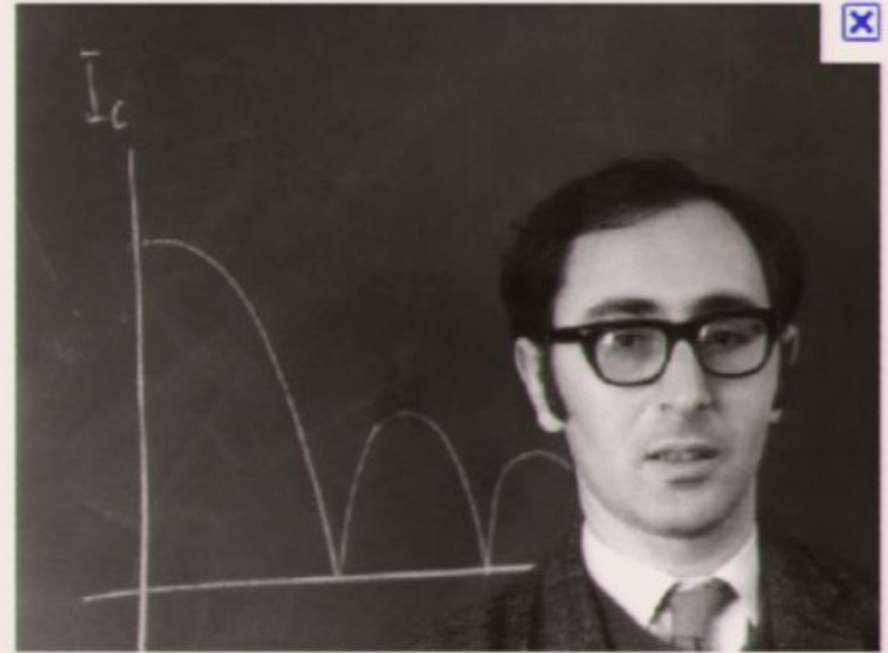
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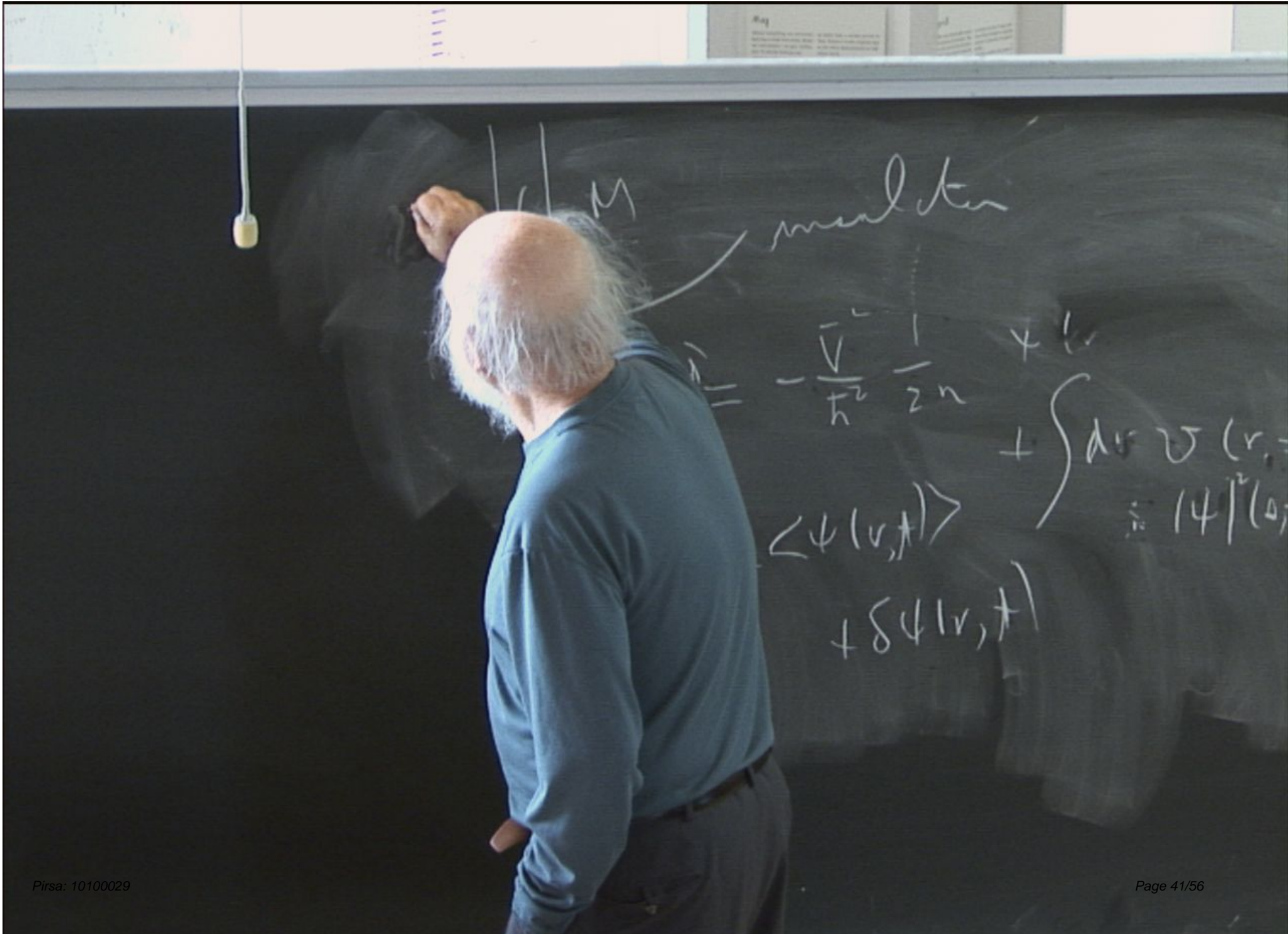
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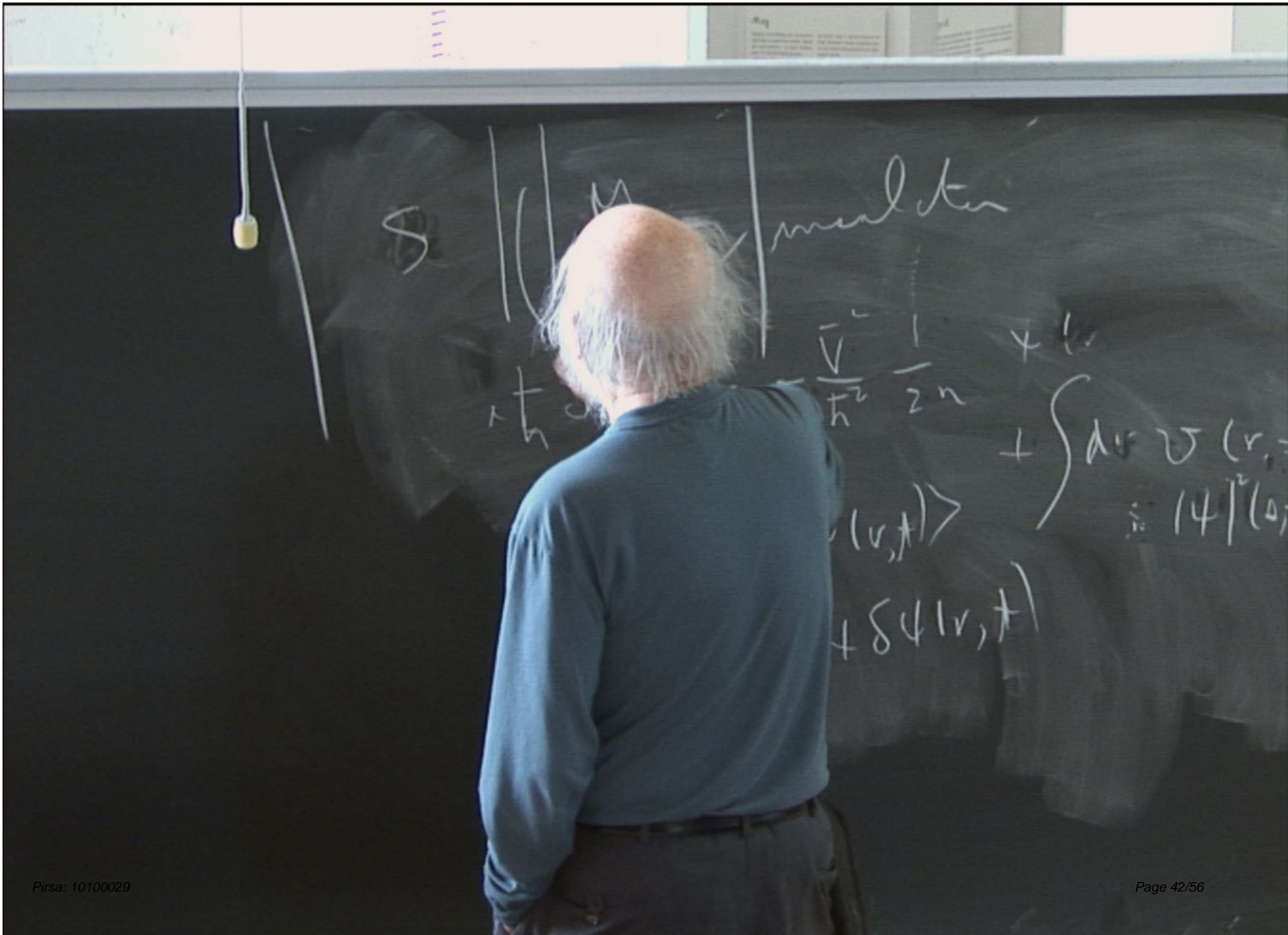
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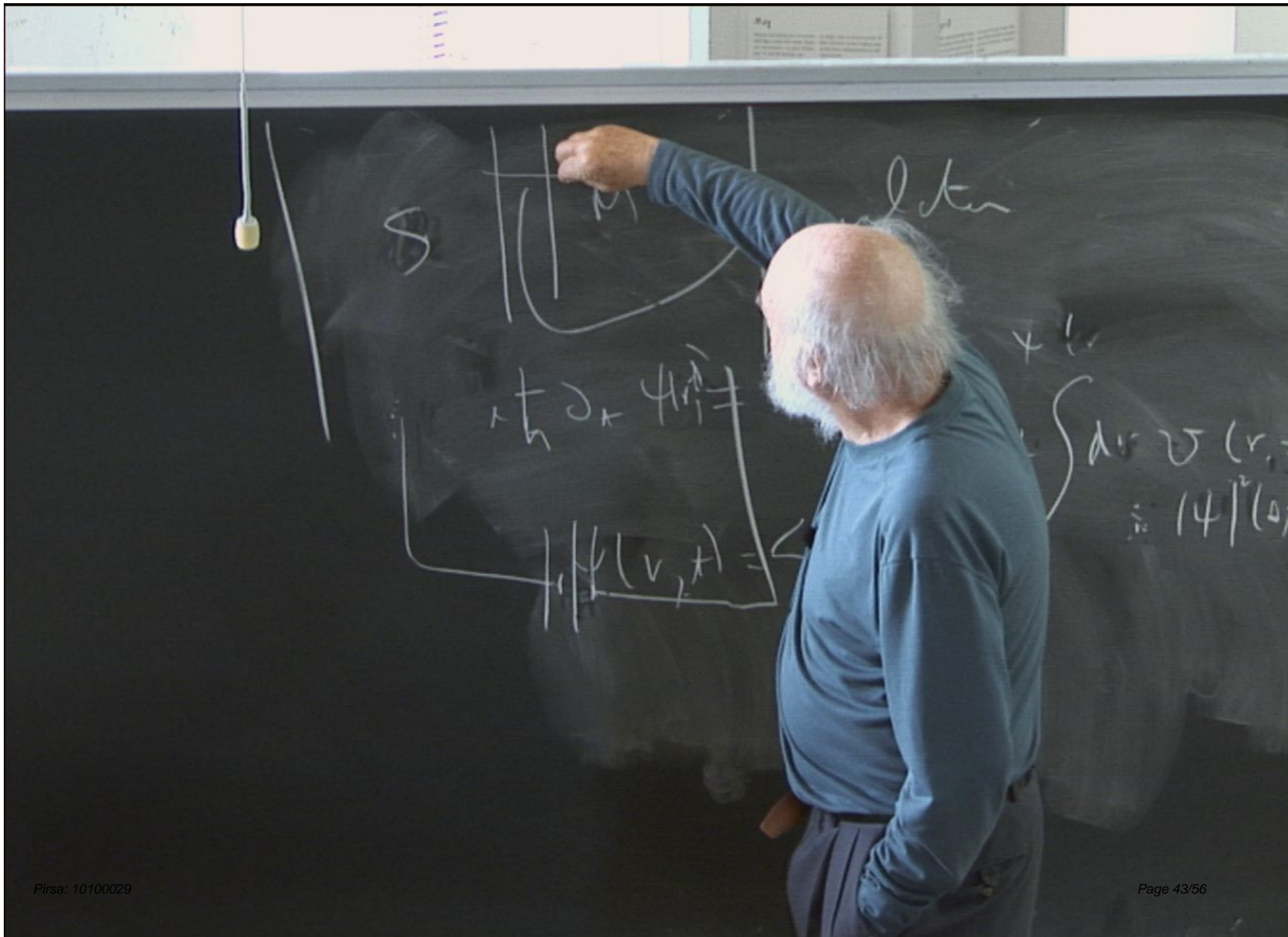
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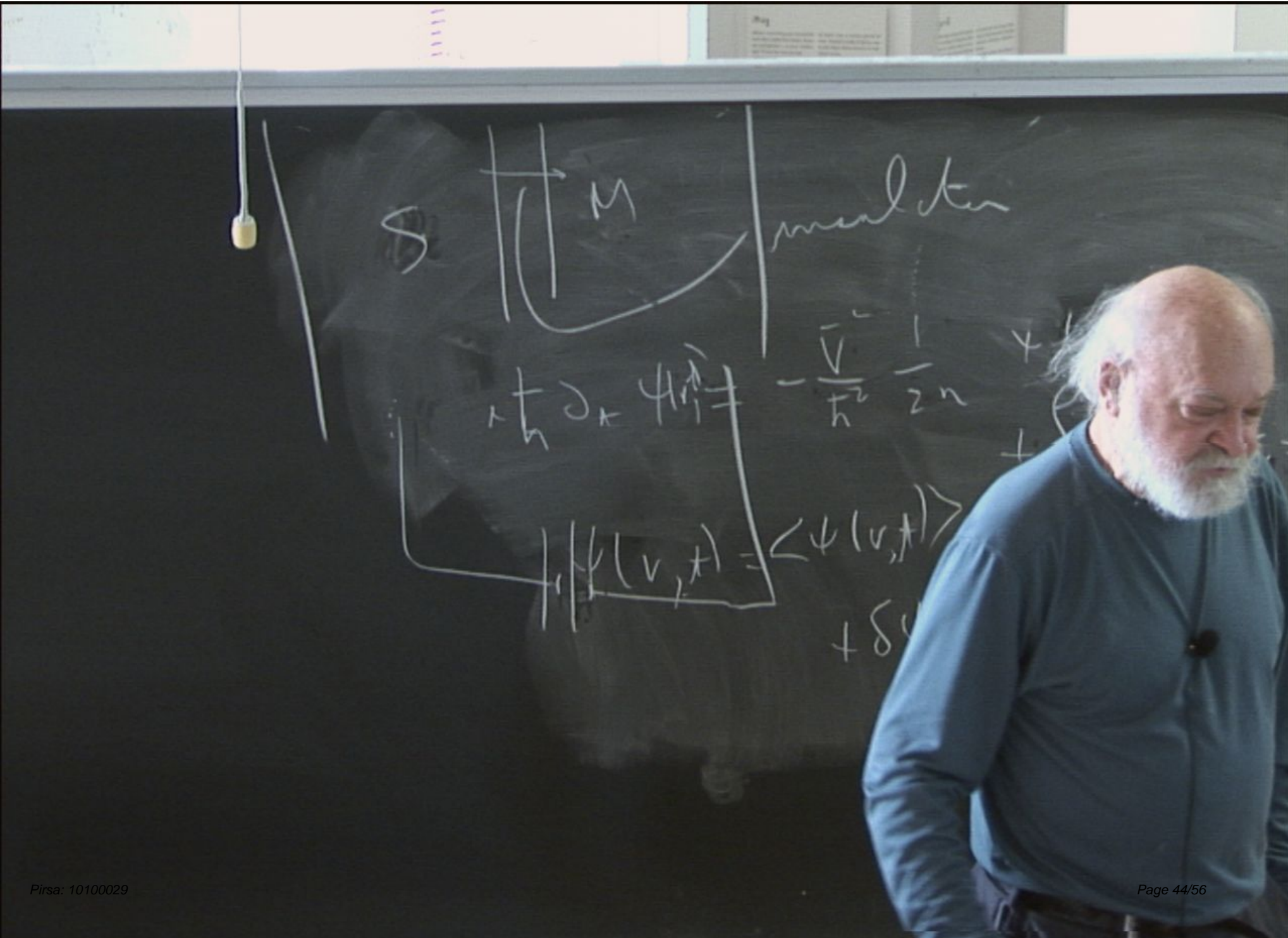
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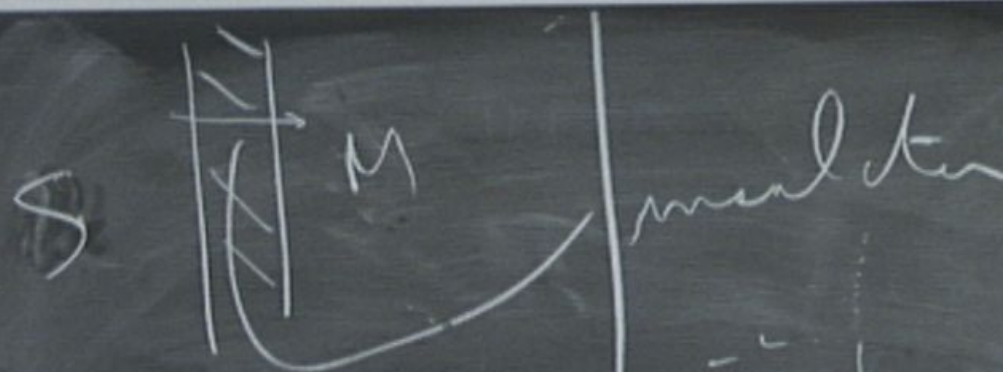
anecdote tells of [Werner Heisenberg](#) and Dirac sailing on a cruise ship to a conference in Japan in August 1929. "Both still in their twenties, and unmarried, they made an odd couple. Heisenberg was a ladies' man who instantly flirted and danced, while Dirac—'an Edwardian geek', as [biographer] Graham Farmelo puts it—suffered agonies if forced into any kind of socialising or small talk. 'Why do you dance?' Dirac asked his companion. 'When there are nice girls, it is a pleasure,' Heisenberg replied. Dirac pondered this notion, then blurted out: 'But, Heisenberg, how do you know beforehand that the girls are nice?'"[







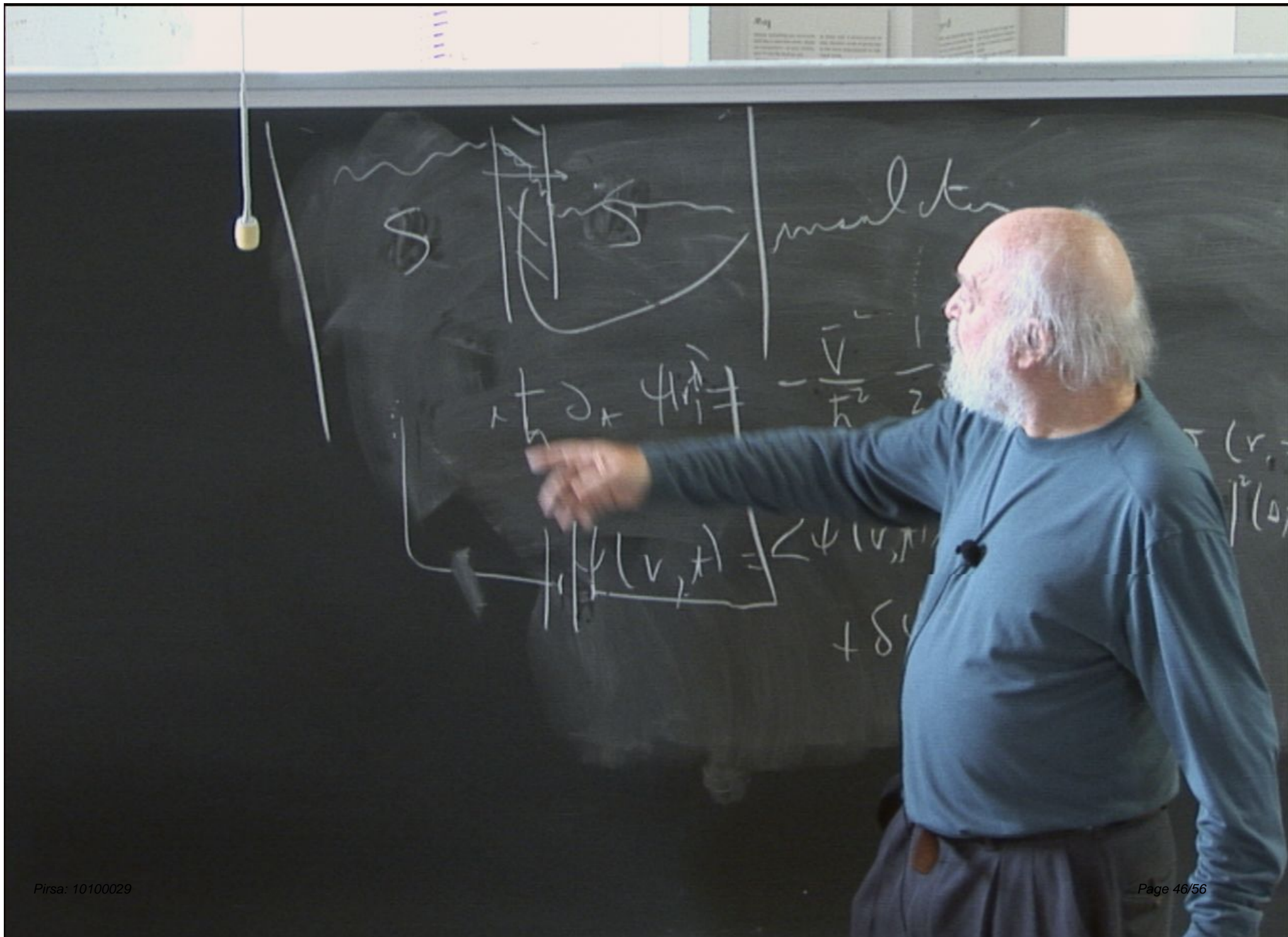


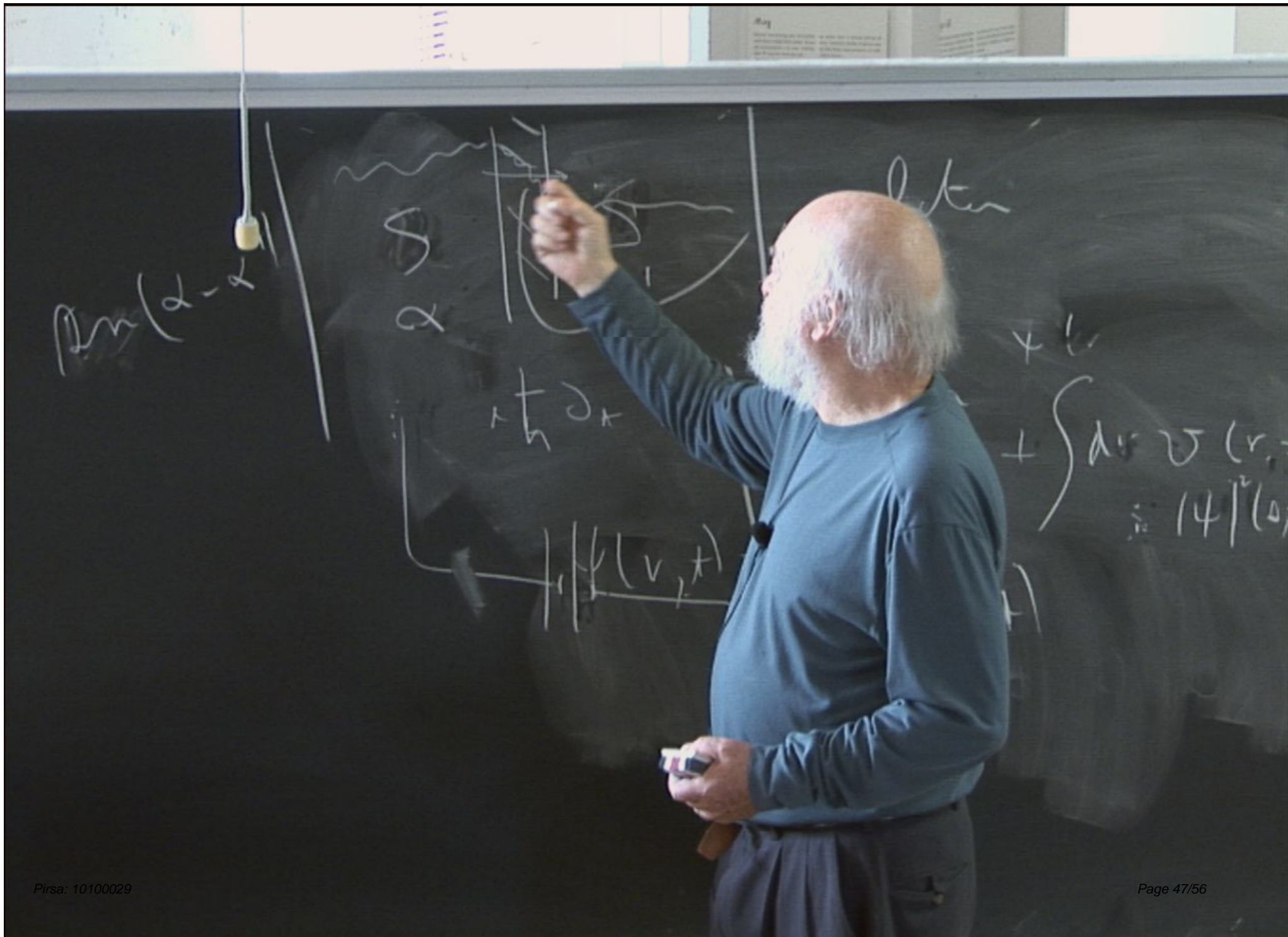


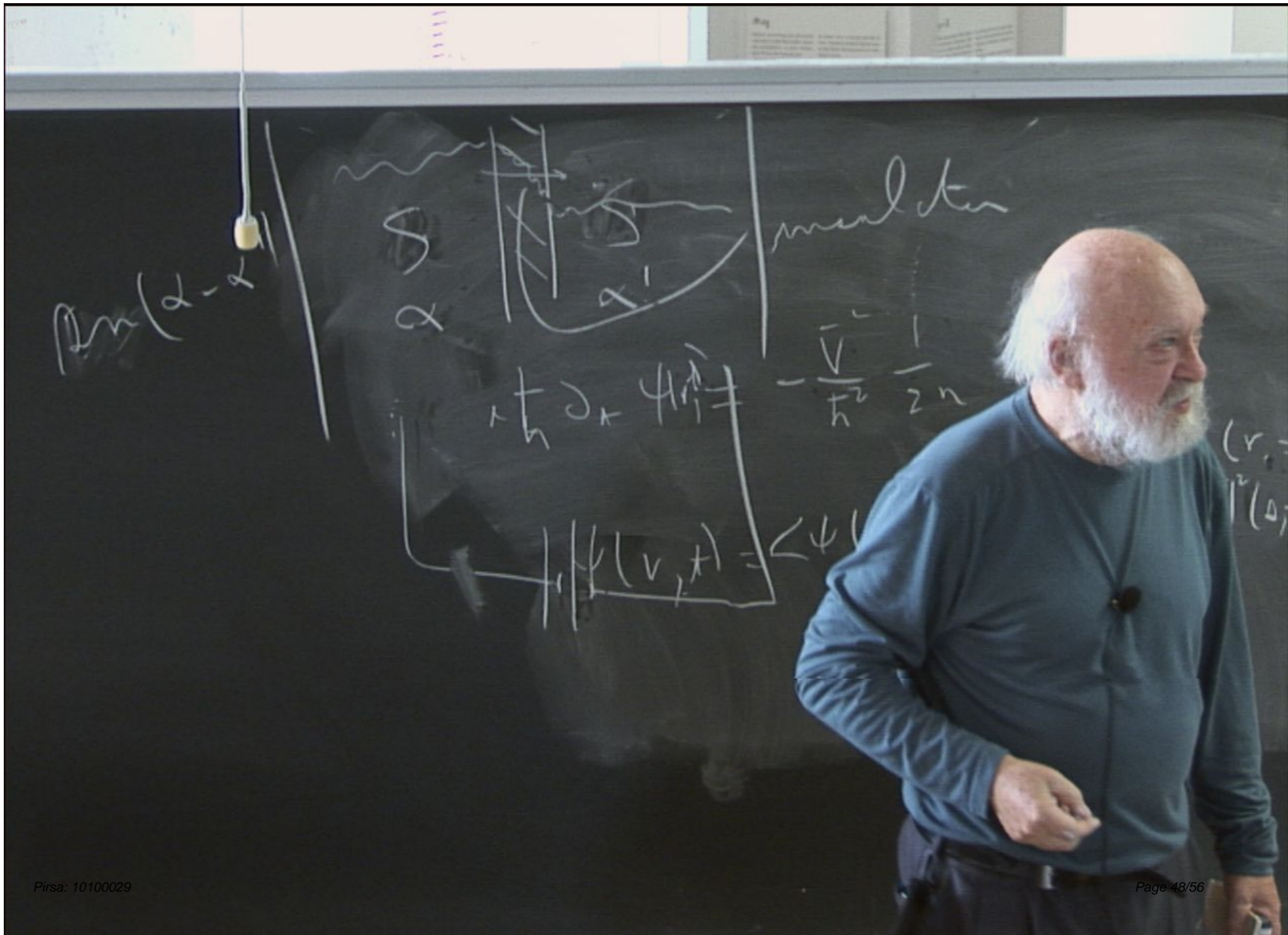
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$$+ \int dr \psi(r,t) = |\psi|^2(t)$$

$$|\psi(r,t)| = \langle \psi(r,t) \rangle + \delta \psi(r,t)$$







Brian Josephson high point at age 23

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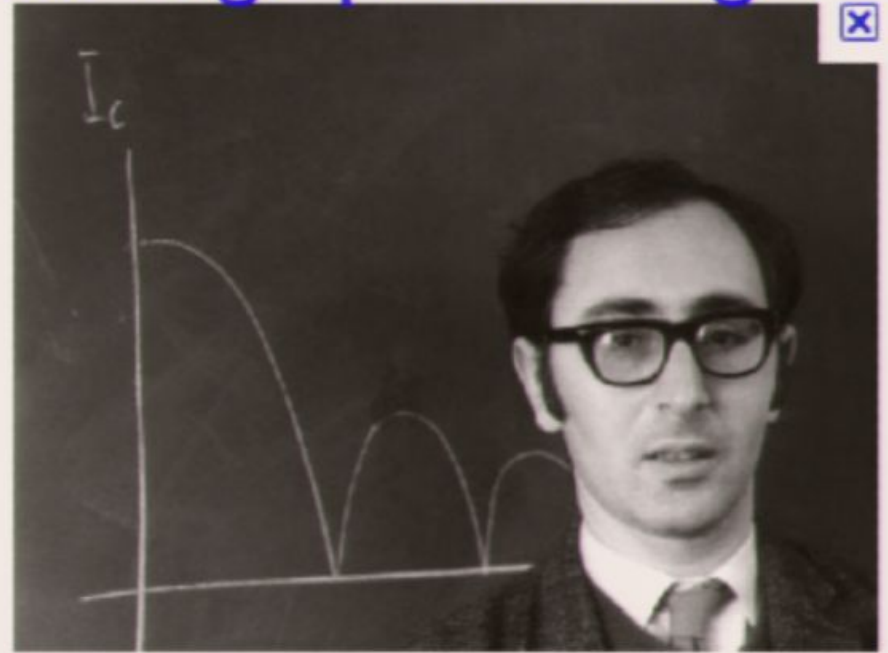
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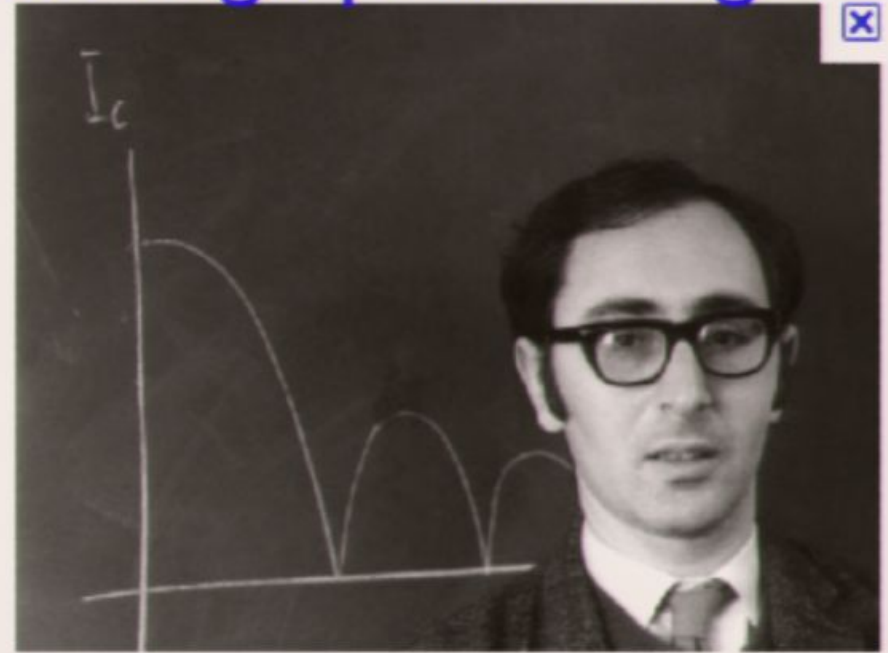
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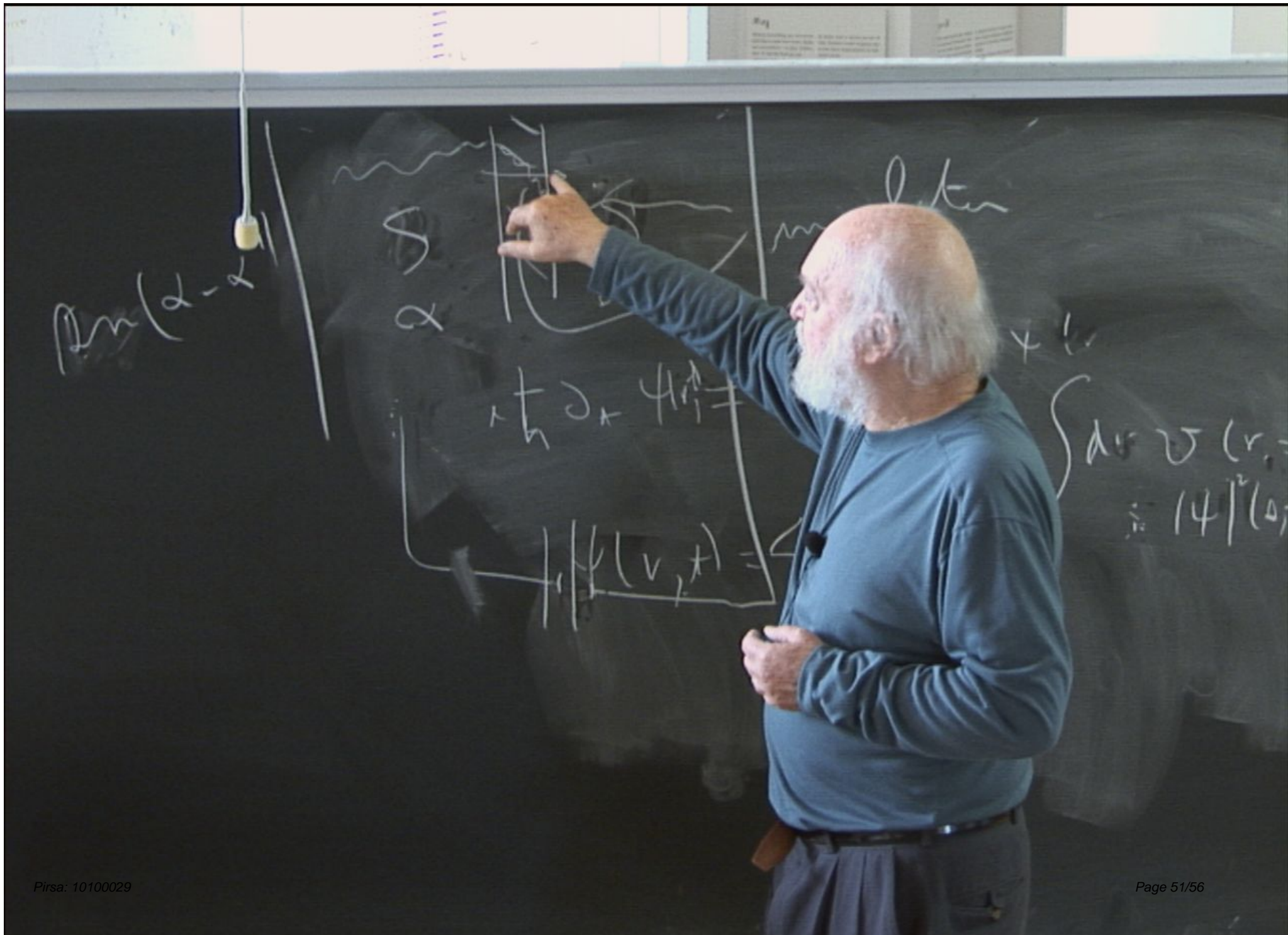
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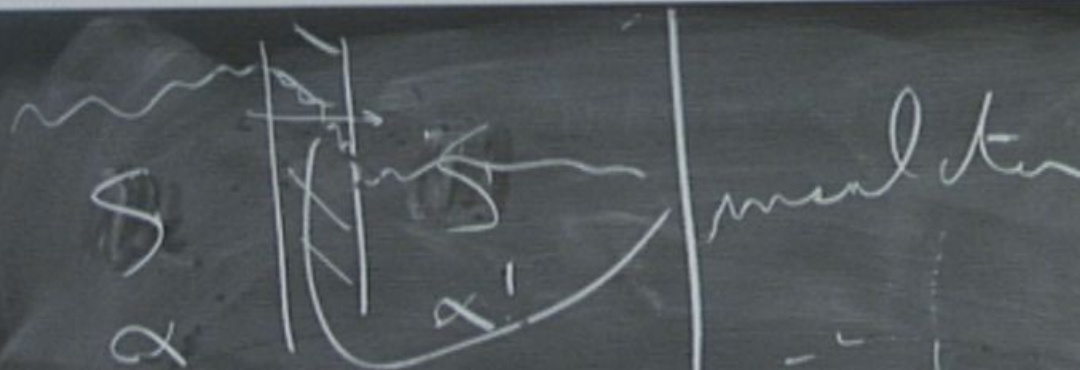
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$\Psi(x-x)$



$$\frac{1}{h} \partial_x \psi(x) =$$

$$-\frac{\bar{V}}{h^2} \frac{1}{2n} + \dots$$

$$+ \int dx \psi(x) \dots$$

$$\psi(x,t) = \langle \psi(x,t) \rangle + \delta \psi(x,t)$$

Brian Josephson high point at age 23

& Harwell

unneling

DC Josephson effect

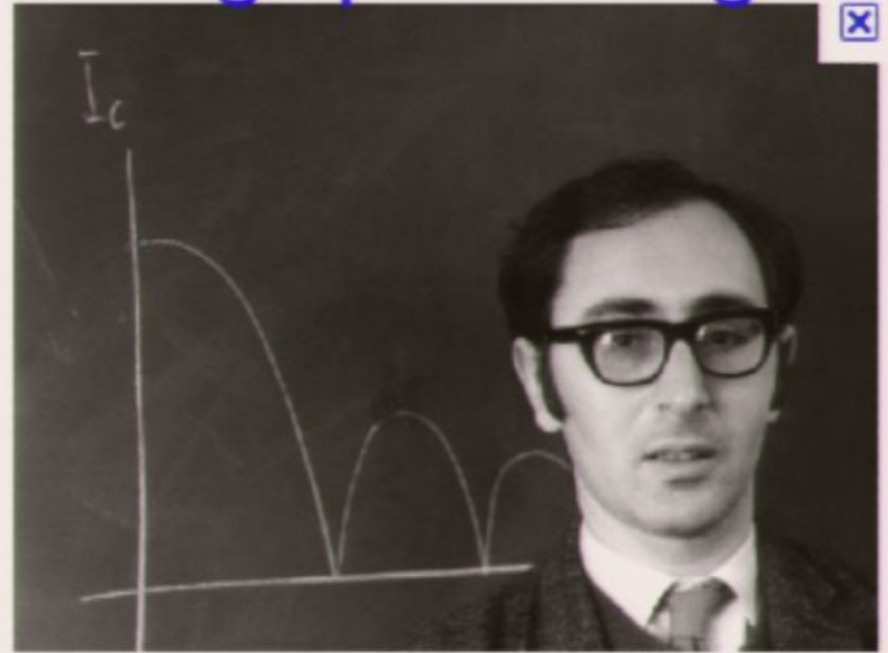
AC Josephson effect

Bardeen

The Mahareshee

The King of Belgium

t The Mahareshee's



Josephson, B.D., 1964: "Coupled Superconductors", *Review of Modern Physics*, **36** [1P1].

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For superconductor

$$F = \int dr \{ t |\psi|^2 + c |\psi|^4 + | [p - 2eA(r,t)] \psi |^2 \}$$
$$p = \hbar \nabla / i$$

Minimize with respect to the condensate wave function.
 ψ . Current is the derivative of F with respect to $A(r,t)$

$$\alpha \psi + \beta |\psi|^2 \psi + \frac{1}{2m} (-i\hbar \nabla - 2e\mathbf{A})^2 \psi = 0$$
$$\mathbf{j} = \frac{2e}{m} \text{Re} \{ \psi^* (-i\hbar \nabla - 2e\mathbf{A}) \psi \}$$

Note that the theory includes F , so when there are several solutions, we can pick the right one.

But back to phase transition, per se

Sound

Mean field theory was in trouble after 1937

Additional Information about fluctuations

Even as far back as 1937, there was evidence of divergent fluctuations near the critical point, as evidenced by **critical opalescence**. As a clear fluid is brought near the critical point, it becomes cloudy.

Smoluchowski (1908) and then **Einstein** (1910) argued that fluctuations in density in the fluid produced scattering and that these fluctuations would diverge at the critical point causing a divergence in the compressibility of the fluid.

A little later, **Ornstein** and **Zernike** (1914, 1916) argued that it was not the magnitude of the local fluctuations which would diverge near criticality. Instead the typical size of the fluctuation region, **the coherence length, ξ** , would diverge as the critical point was approached. That divergence would produce the infinity in the susceptibility. Specifically the divergence would appear in a correlation function

$$\langle [\rho(\mathbf{x}) - \langle \rho \rangle] [\rho(\mathbf{y}) - \langle \rho \rangle] \rangle = (1/|\mathbf{x} - \mathbf{y}|) \exp(-|\mathbf{x} - \mathbf{y}|/\xi)$$

How could these divergences occur? Mean field theory does roughly predicts them, but its detailed predictions are incorrect