Title: Statistical Mechanics (PHYS 602) - Lecture 8

Date: Oct 07, 2009 10:30 AM

URL: http://pirsa.org/09100129

Abstract:

$$X = \sum_{j=1}^{M} \sigma_j$$

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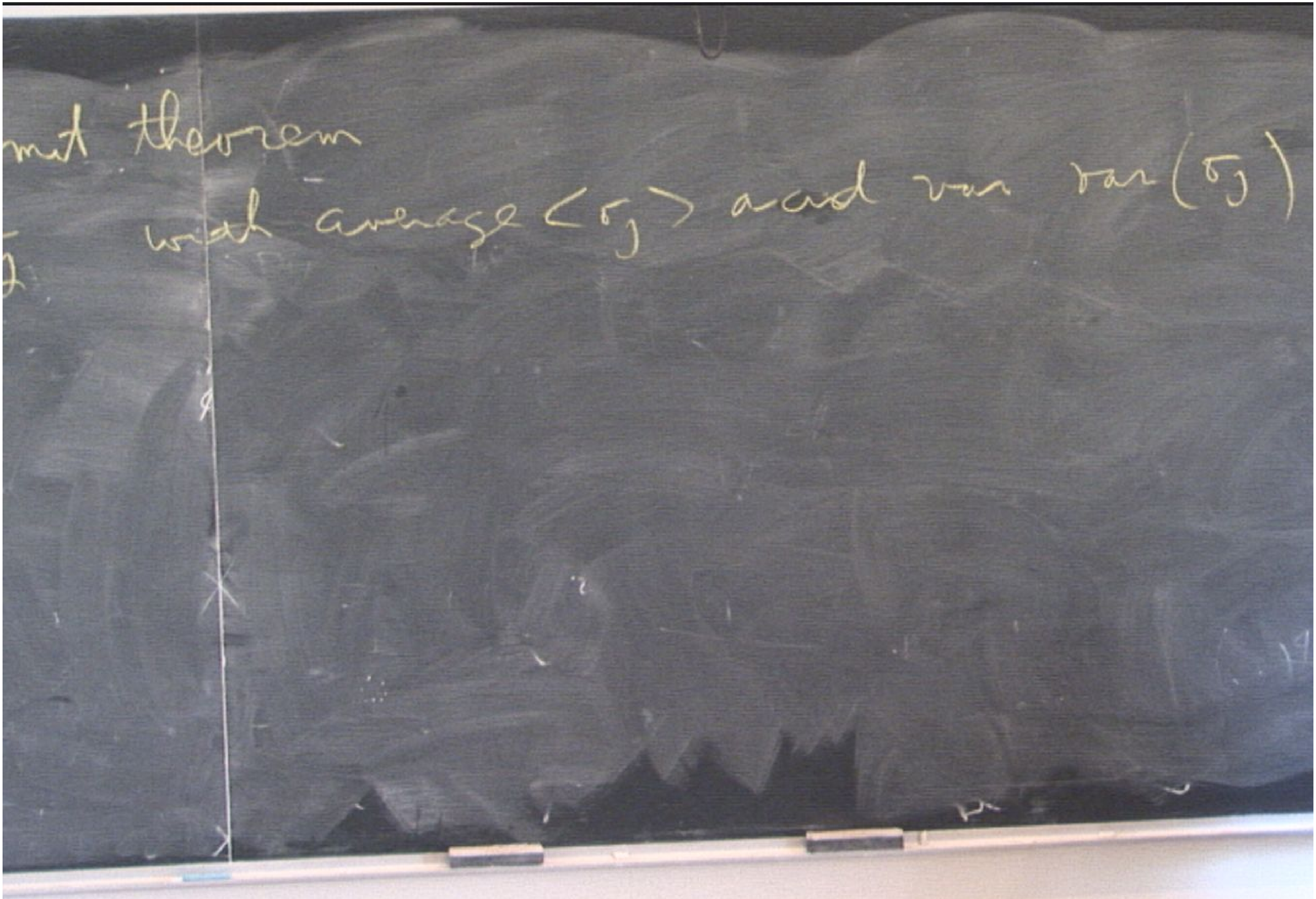
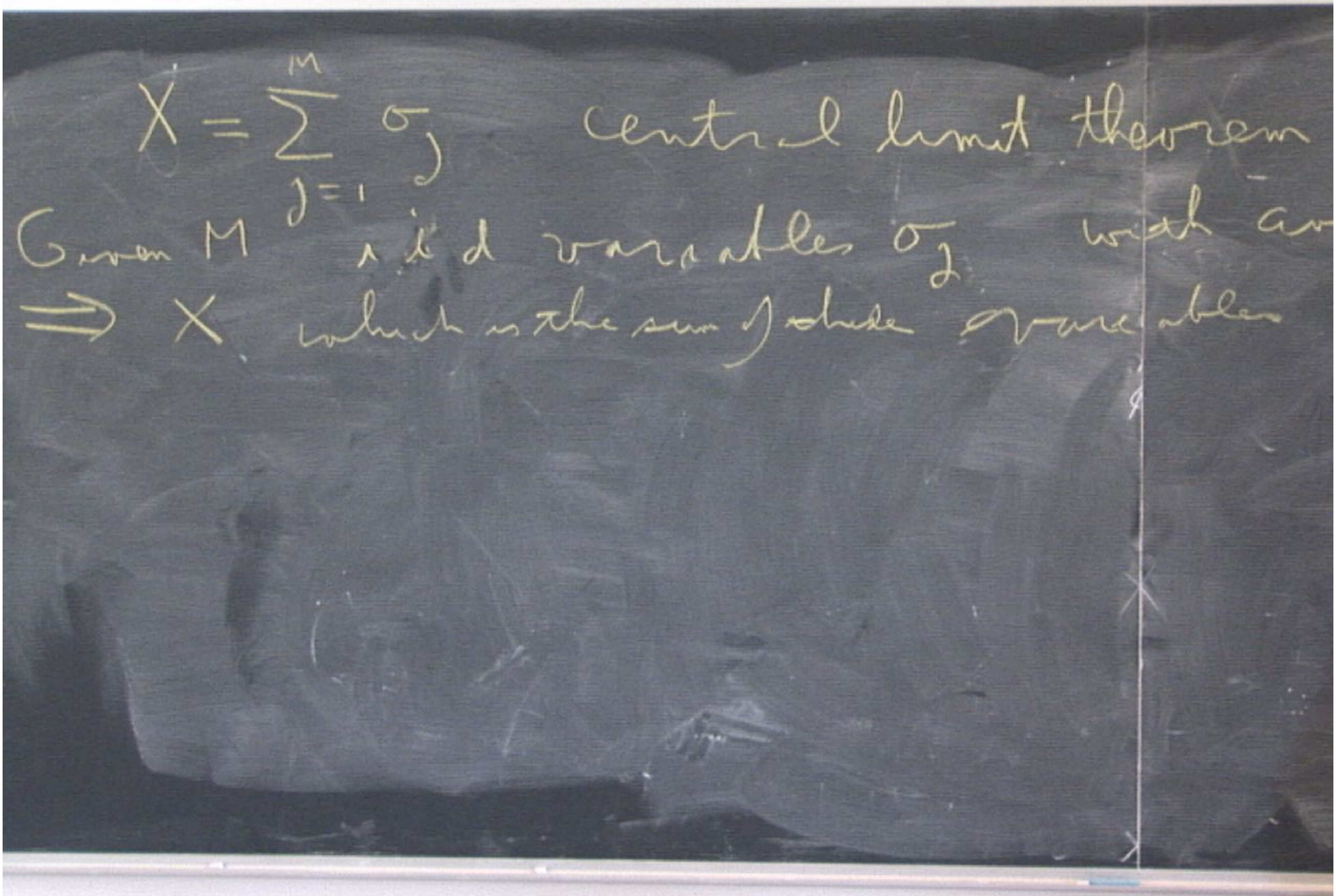
central limit theorem

Given M iid variables σ_j



mit theorem

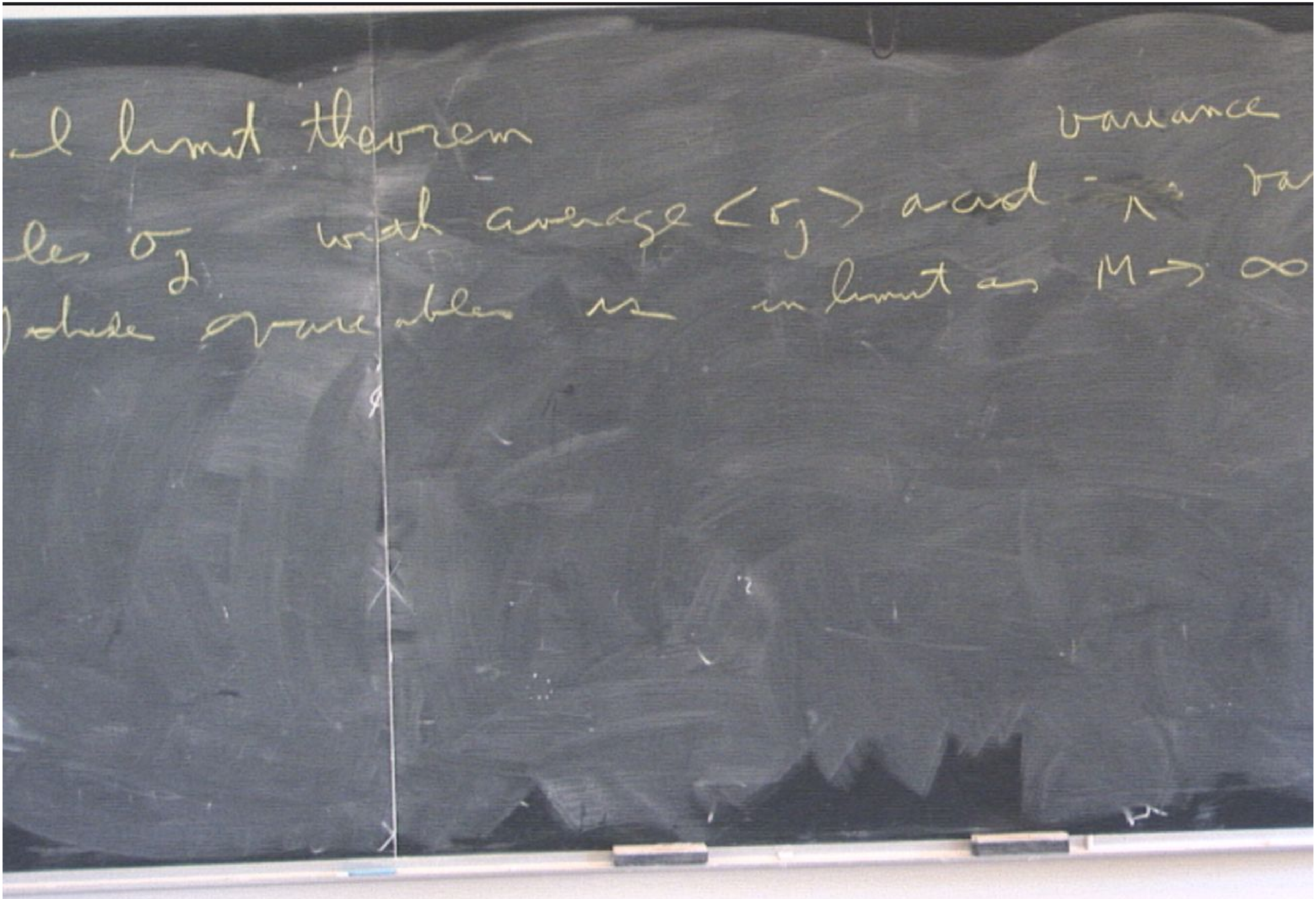
with average $\langle \sigma_j \rangle$ and var var(σ_j)



$X = \sum_{j=1}^{M} \sigma_j$ central limit theorem

Given M i.i.d variables σ_j with av

$\Rightarrow$ X which is the sum of these variables

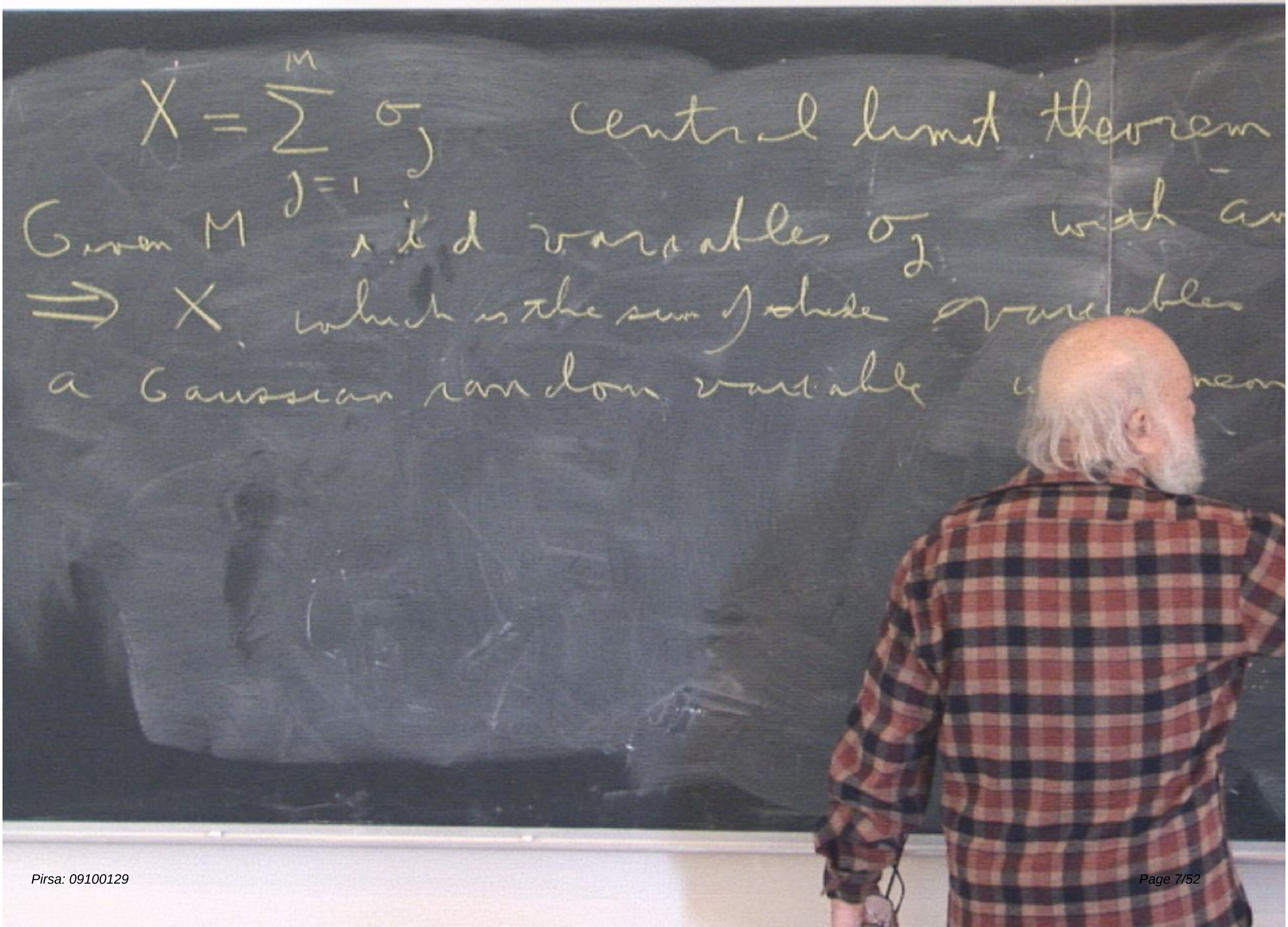


l limit theorem variance

les σ_j with average $\langle\sigma_j\rangle$ and $\hat{\ }$ va

∂ in limit as $M \to \infty$

)clude variables is

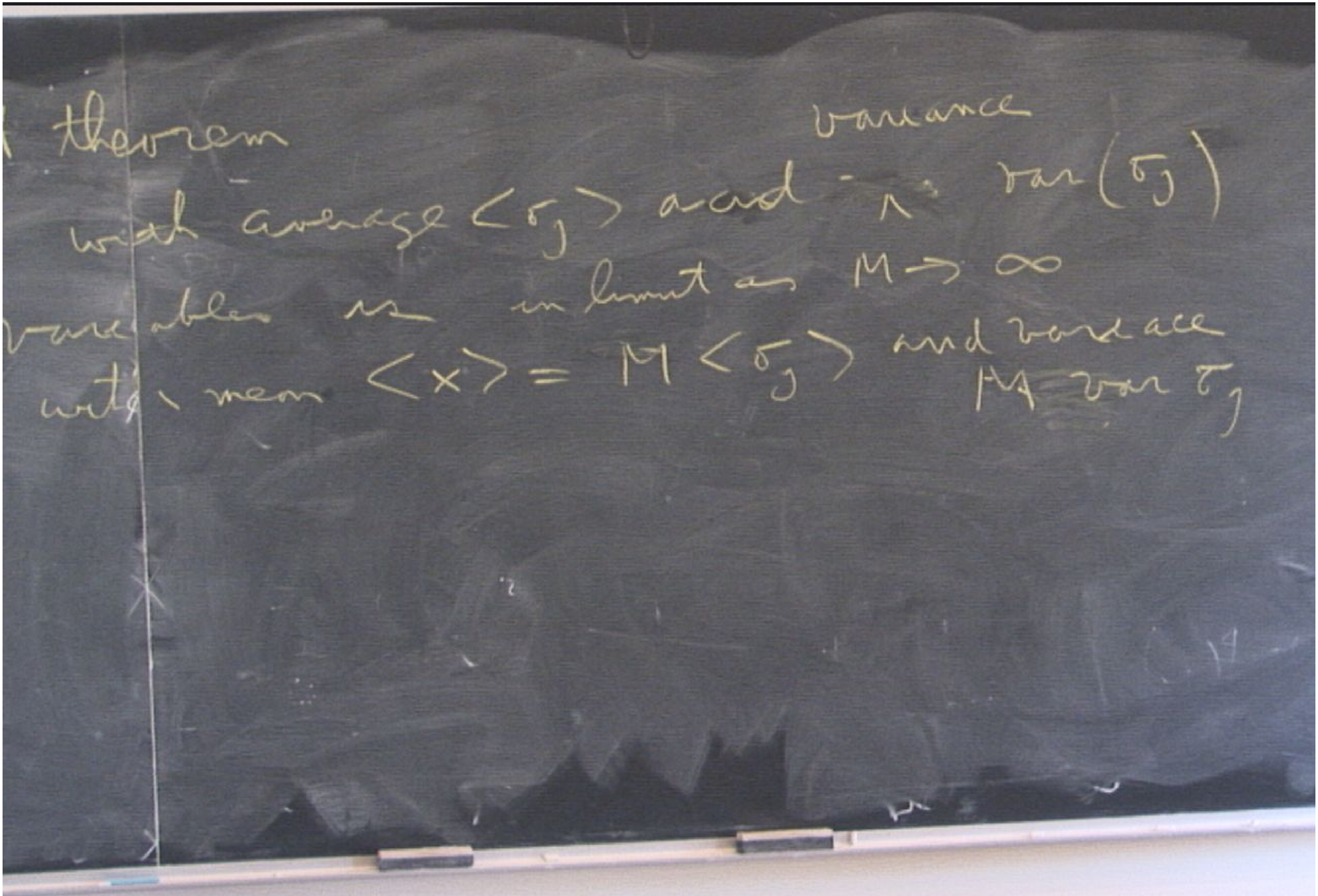


$$X = \sum_{j=1}^{M} \sigma_j$$ central limit theorem

Given M i.i.d variables σ_j with a

$\Rightarrow$ X which is the sum of these variables

a Gaussian random variable mean

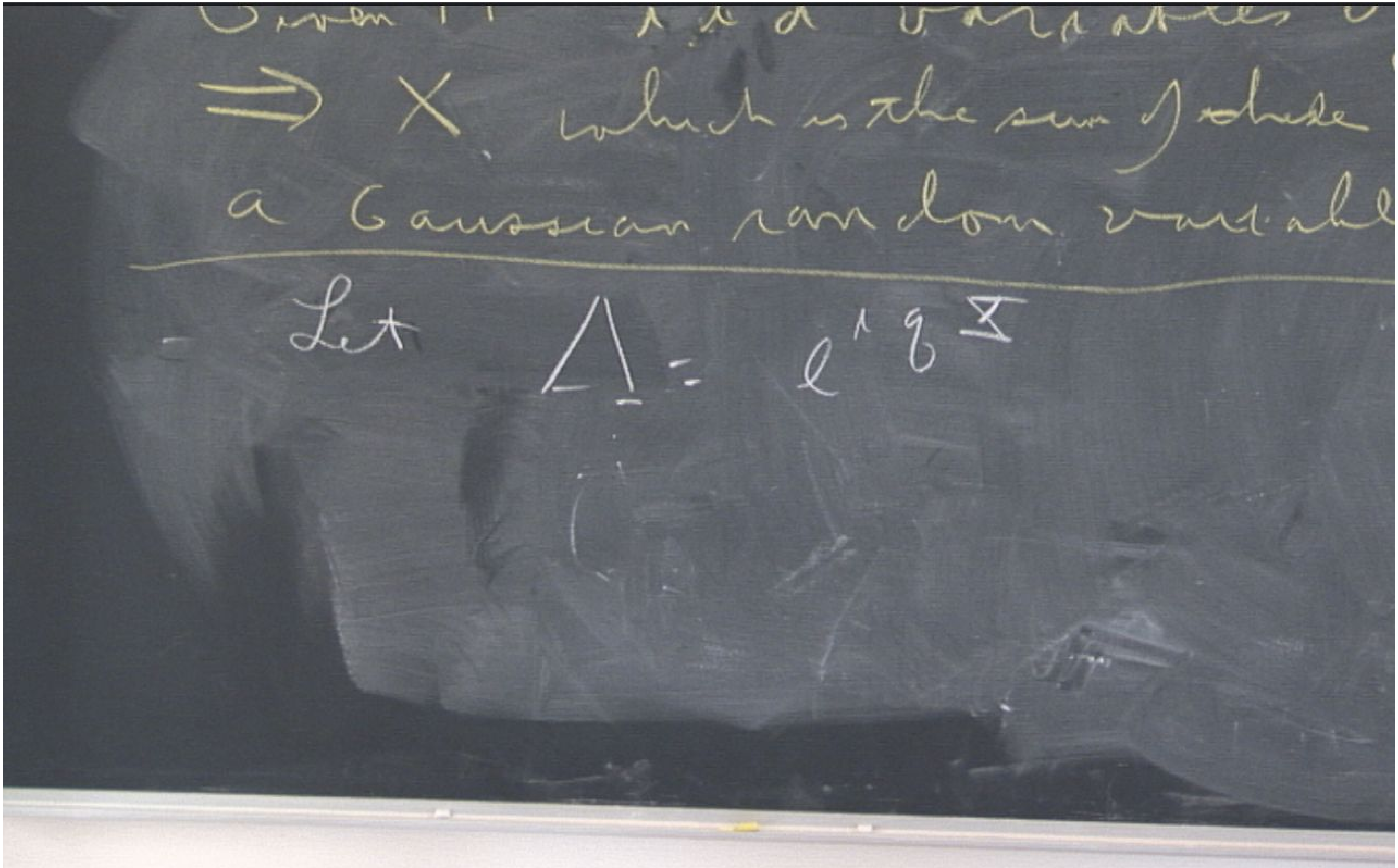


theorem variance

with average $\langle \sigma_j \rangle$ and $\mathrm{var}(\sigma_j)$

variables is in limit as $M \to \infty$

with mean $\langle x \rangle = M \langle \sigma_j \rangle$ and variance $M \,\mathrm{var}\, \sigma_j$

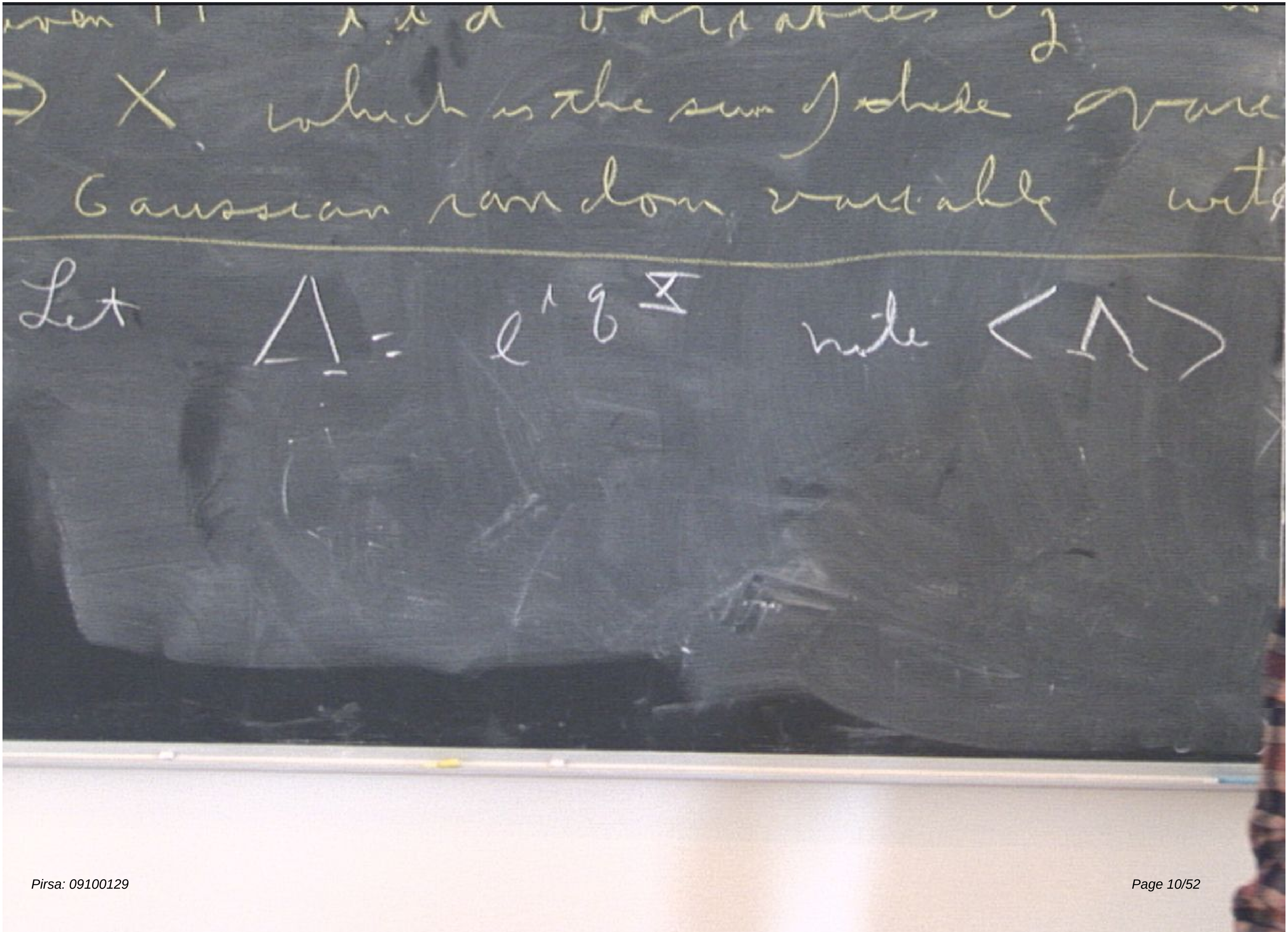


Given N i.i.d variables

$\Rightarrow$ X which is the sum of those

a Gaussian random variable

Let $\underline{\Delta} = e^{i q X}$



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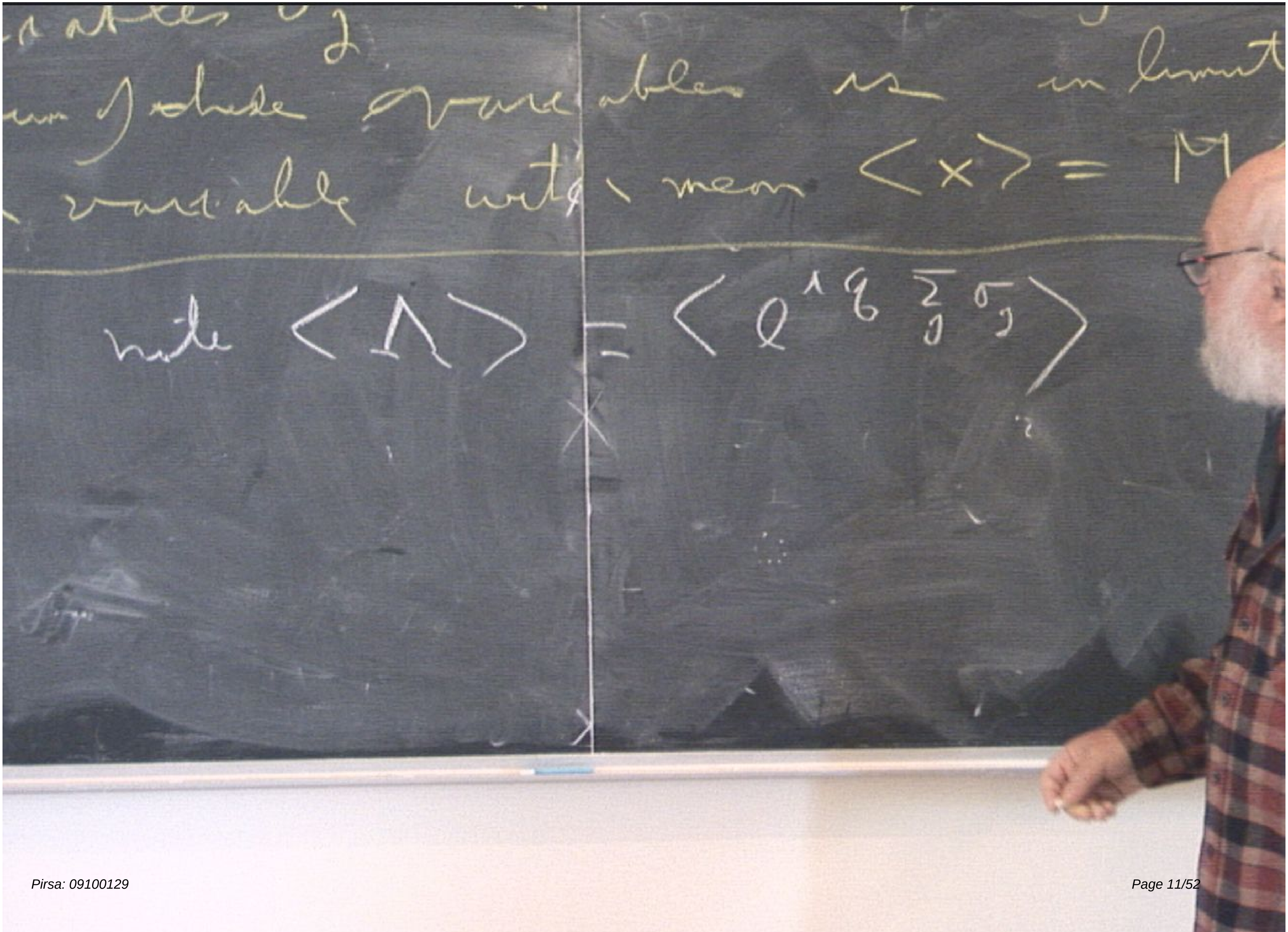
⇒ X which is the sum of these varia

Gaussian random variable wit

Let $\Lambda = e^{iqX}$ write $\langle \Lambda \rangle$

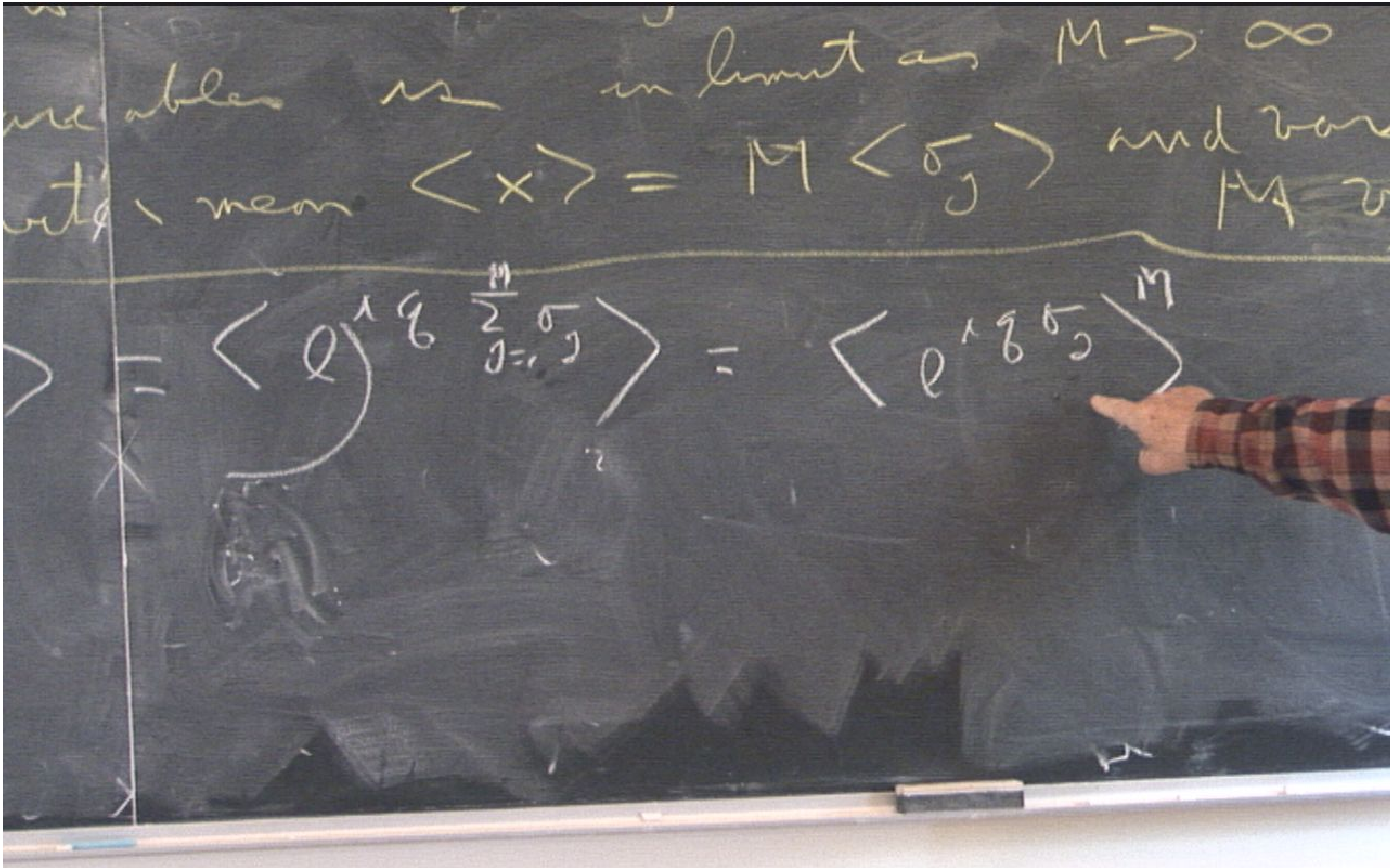


…riables of …

…um of these variables is … in limit

… variable with mean $\langle x \rangle = M$

write $\langle \Lambda \rangle = \langle e^{i \xi \sum_j \sigma_j} \rangle$



ariables as in limit as $M \to \infty$

with mean $\langle x \rangle = M \langle \sigma_j \rangle$ and var

M v

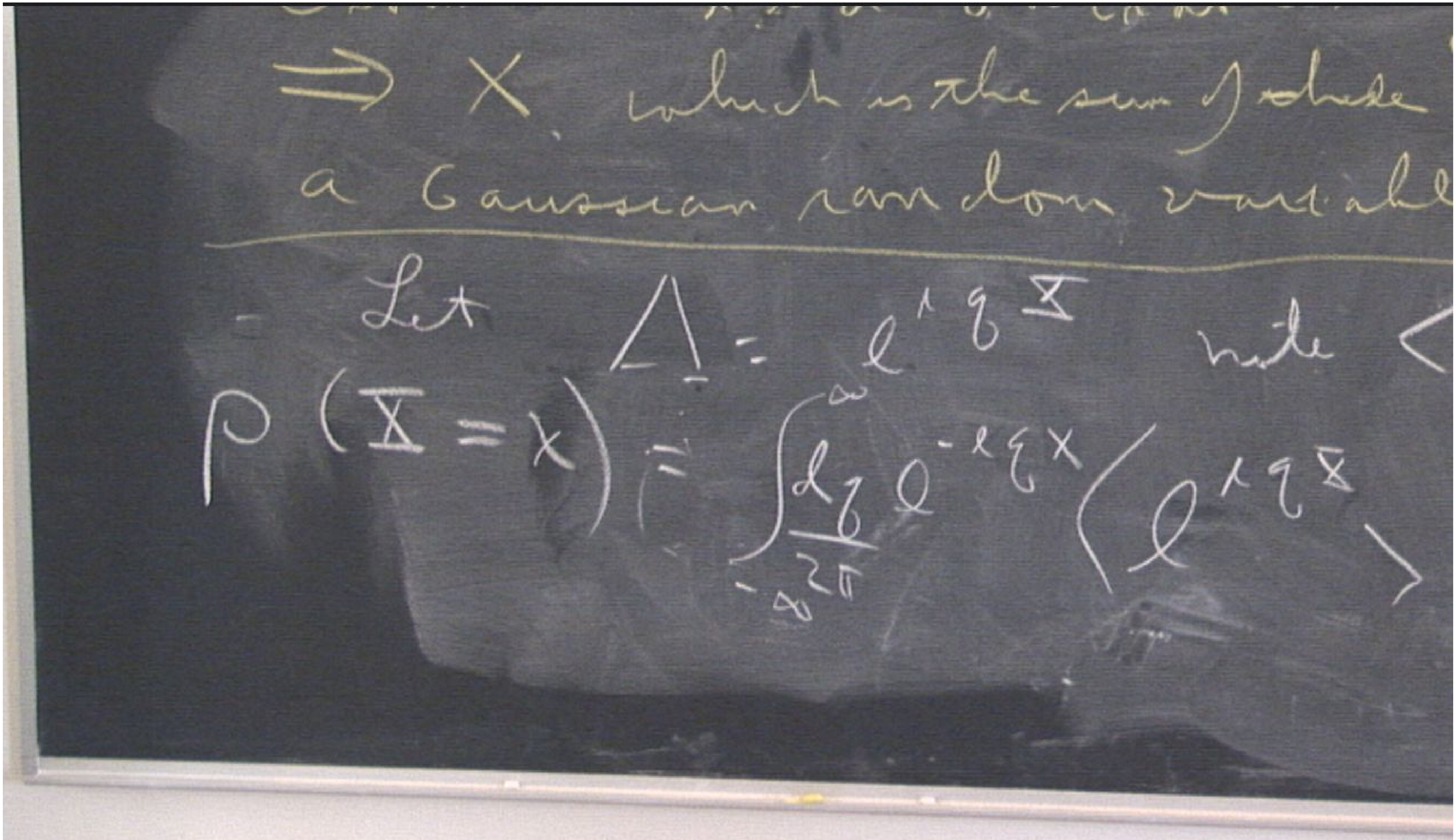
$$\rangle = \langle e^{i\xi \sum_{j=1}^{M} \sigma_j} \rangle = \langle e^{i\xi\sigma_j} \rangle^{M}$$

in limit as $M \to \infty$

$\langle x \rangle = M \langle \sigma_j \rangle$ and variance

M var σ_j

$$\xi \sum_{j=1}^{M} \sigma_j \rangle = \langle e^{i\xi\sigma_j} \rangle^{M} = [f(\xi)]^{M}$$

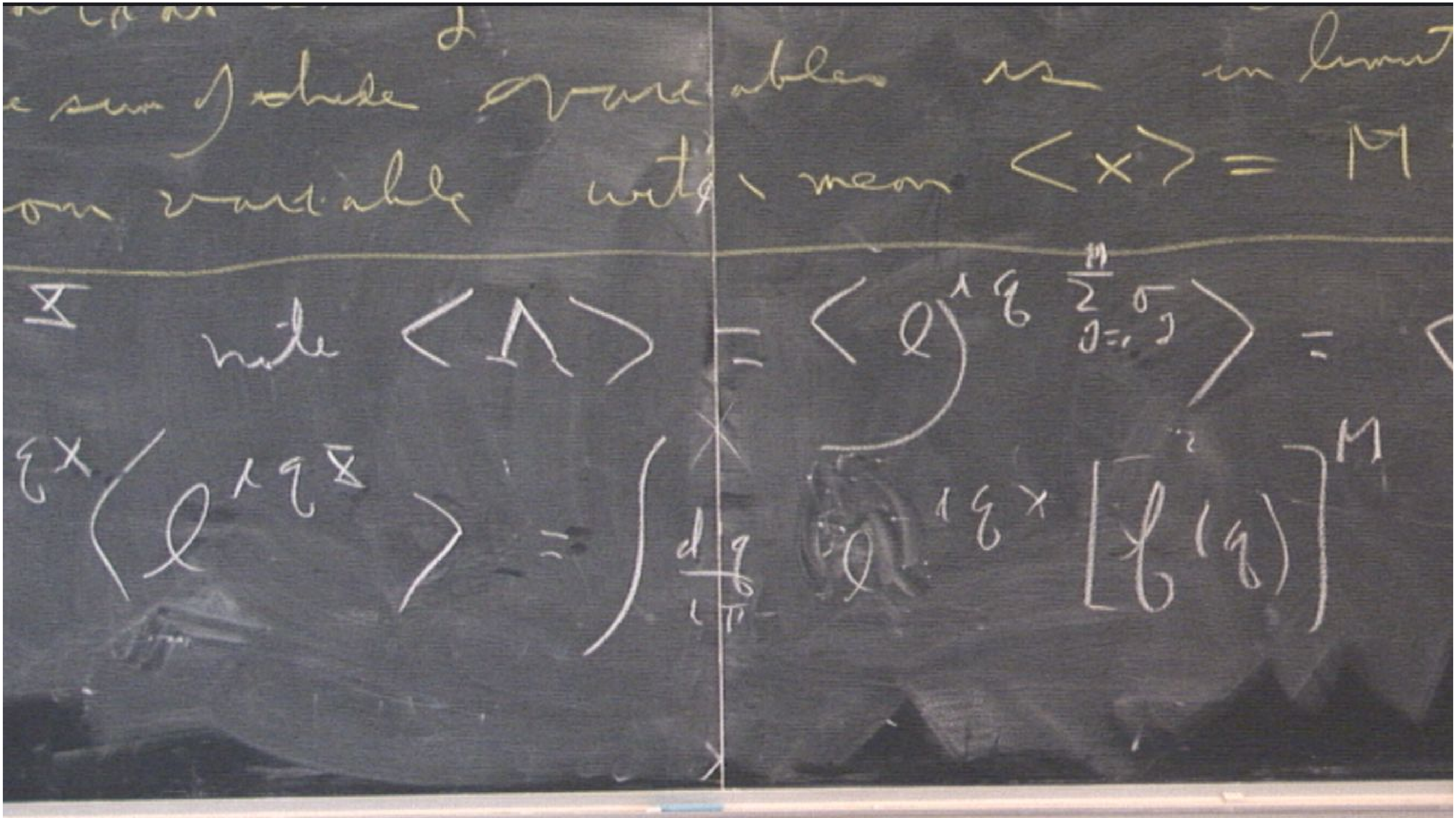


$\Rightarrow$ X which is the sum of whole

a Gaussian random variabl

Let $\Delta = e^{i\xi \mathbb{X}}$ note <

$$\rho(\mathbb{X} = x) = \int_{-\infty}^{\infty} \frac{d\xi}{2\pi} e^{-i\xi x} \langle e^{i\xi \mathbb{X}} \rangle$$

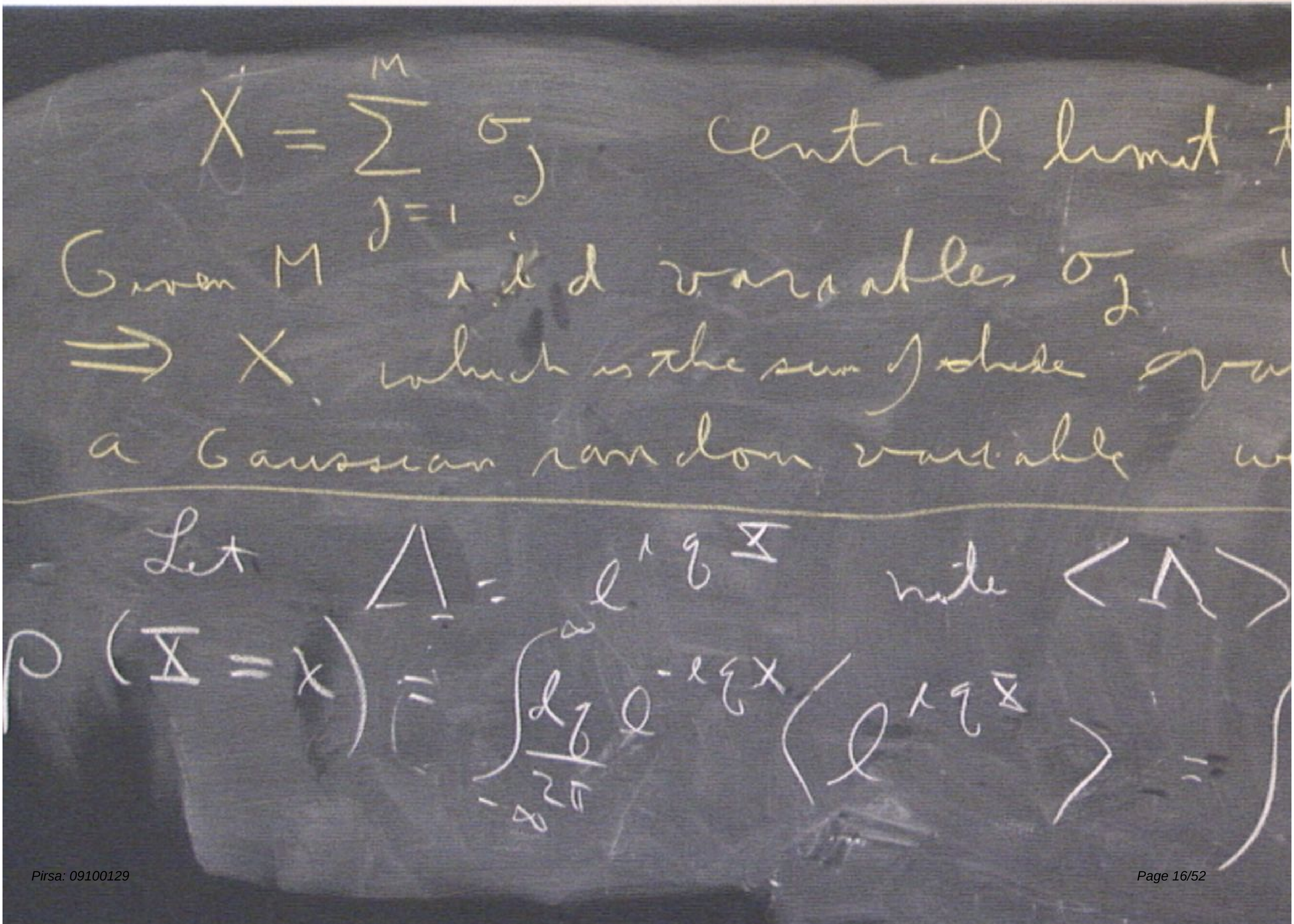


e sum of whole variables is in limit

om variable with mean $\langle x \rangle = M$

X note $\langle \Lambda \rangle = \langle e^{\lambda q \sum_{j=1}^{M} \sigma_j} \rangle =$

$q^{x} \langle e^{\lambda q^{X}} \rangle = \int \frac{dq}{2\pi} e^{i q x} \left[f(q) \right]^{M}$



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$$\rho(X = x) = \int_{-\infty}^{\infty} \frac{d\xi}{2\pi} e^{-i\xi x} \left\langle e^{i \xi X} \right\rangle = \int$$

in limit as M

and variance

$\langle x \rangle = M \langle \sigma_j \rangle$ M var σ_j

$) ^{i\xi \sum_{j=1}^{M} \sigma_j} \rangle = \langle e^{i\xi\sigma_j} \rangle^M = [f(\xi)]^M$

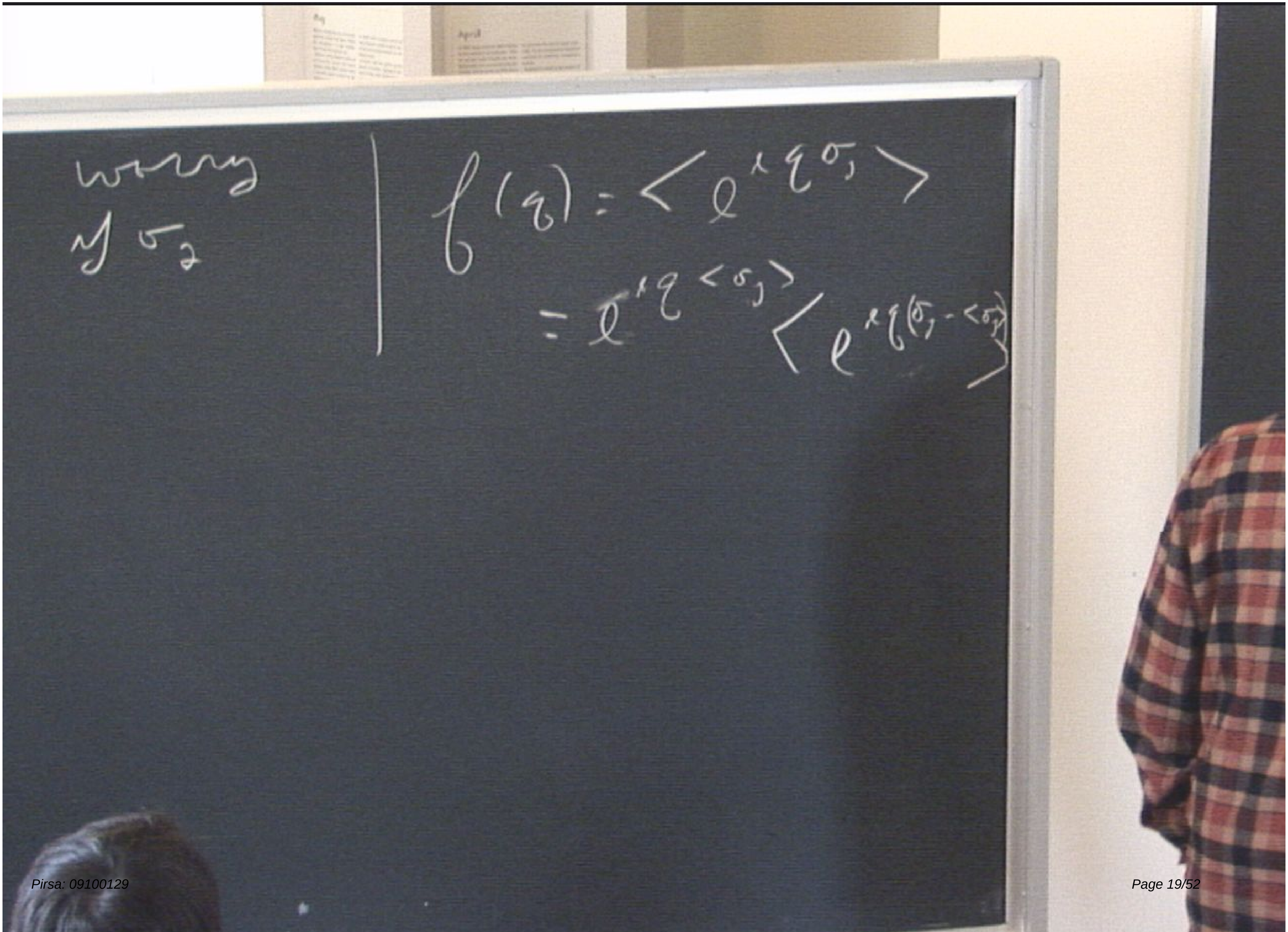
$i\xi x$ $[f(\xi)]^M$ M →

=

cos ξ

$$f(\xi) = \langle e^{i\xi\sigma_j} \rangle$$

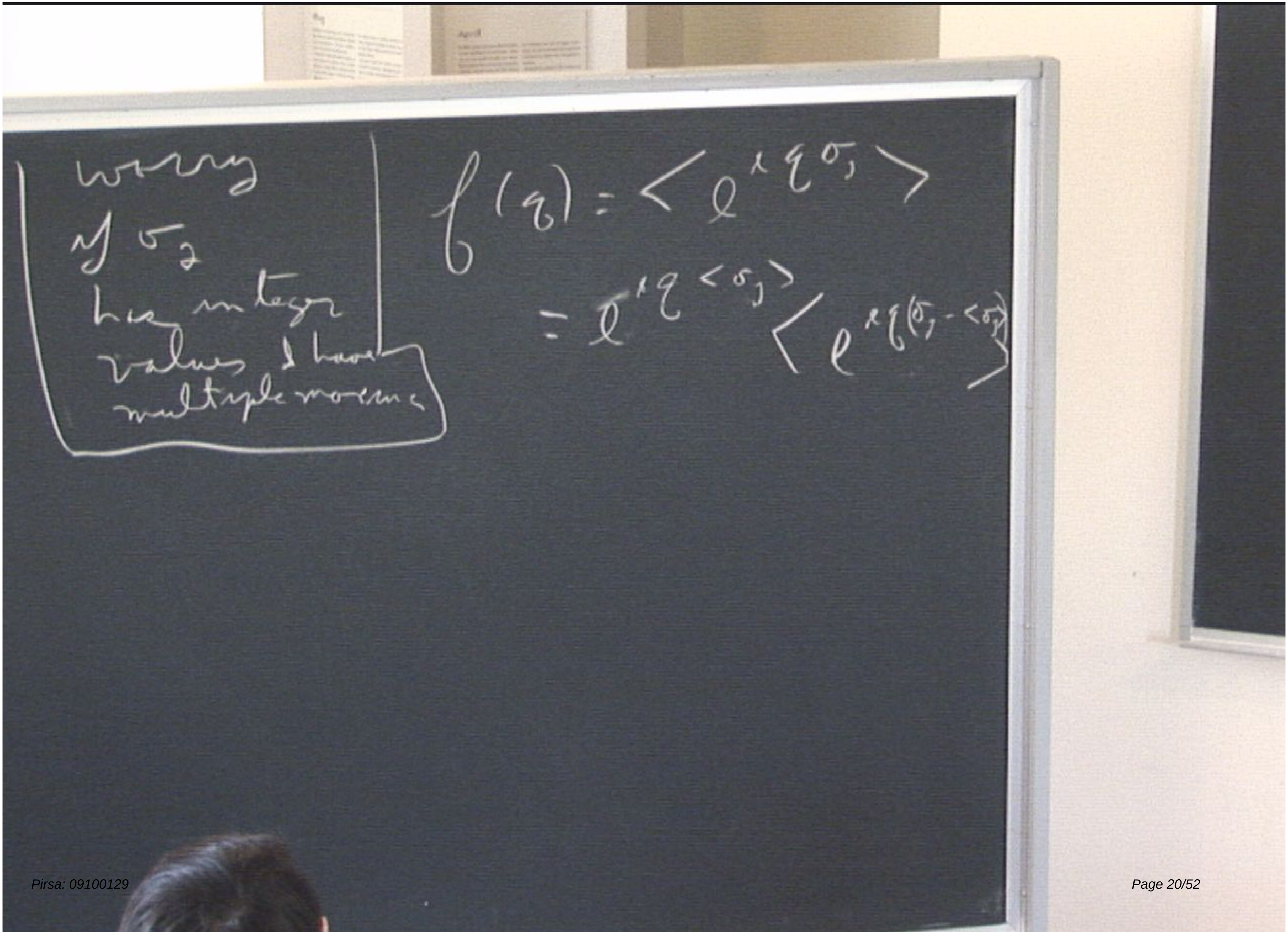
$$= e^{i\xi\langle\sigma_j\rangle} \langle e^{i\xi(\sigma_j - \langle\sigma_j\rangle)} \rangle$$



worry of σ_2

$$f(q) = \langle e^{iq\sigma_j} \rangle$$

$$= e^{iq\langle \sigma_j \rangle} \langle e^{iq(\sigma_j - \langle \sigma_j \rangle)} \rangle$$



worry
if σ_z
has integer
values & have
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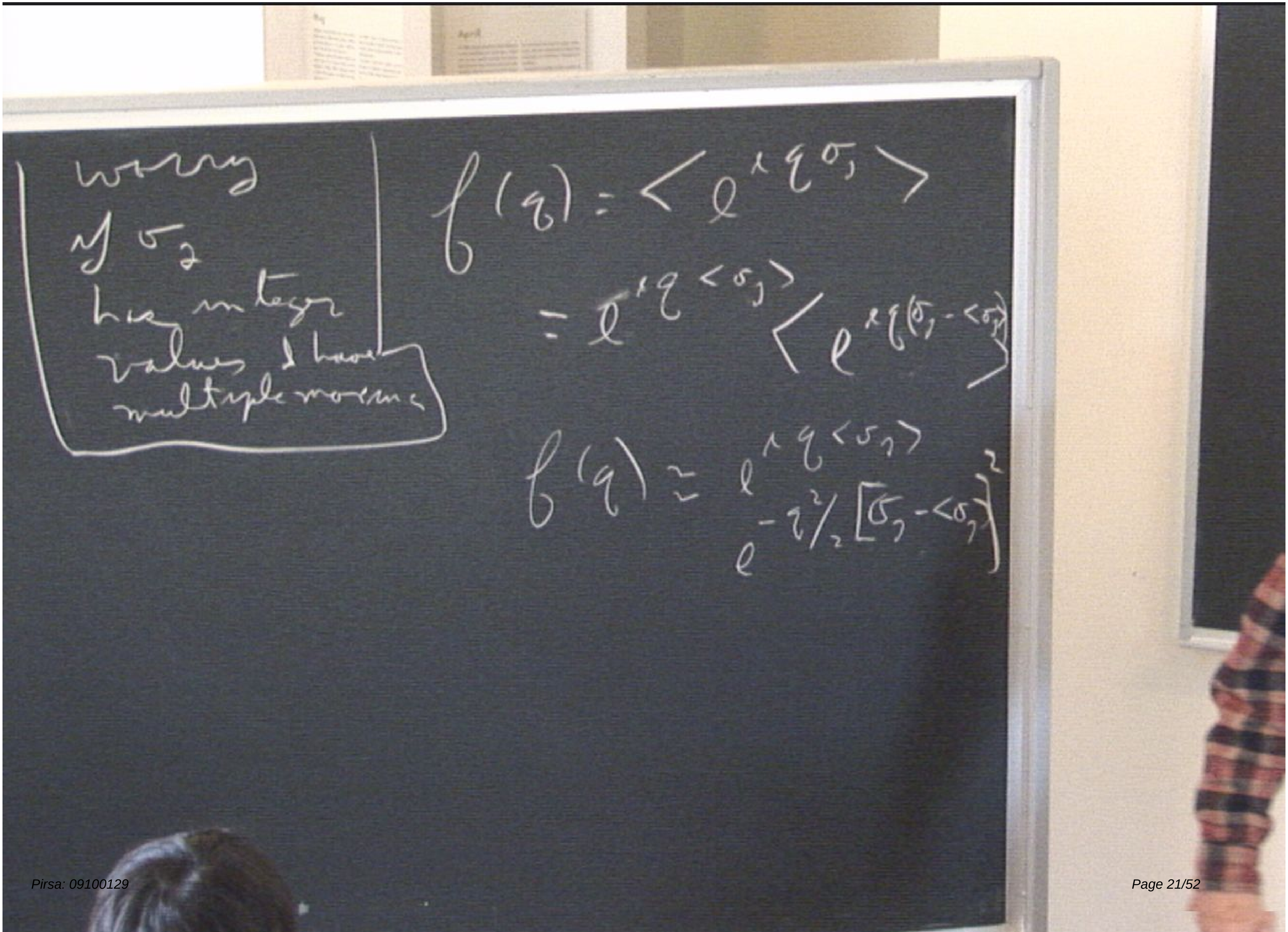

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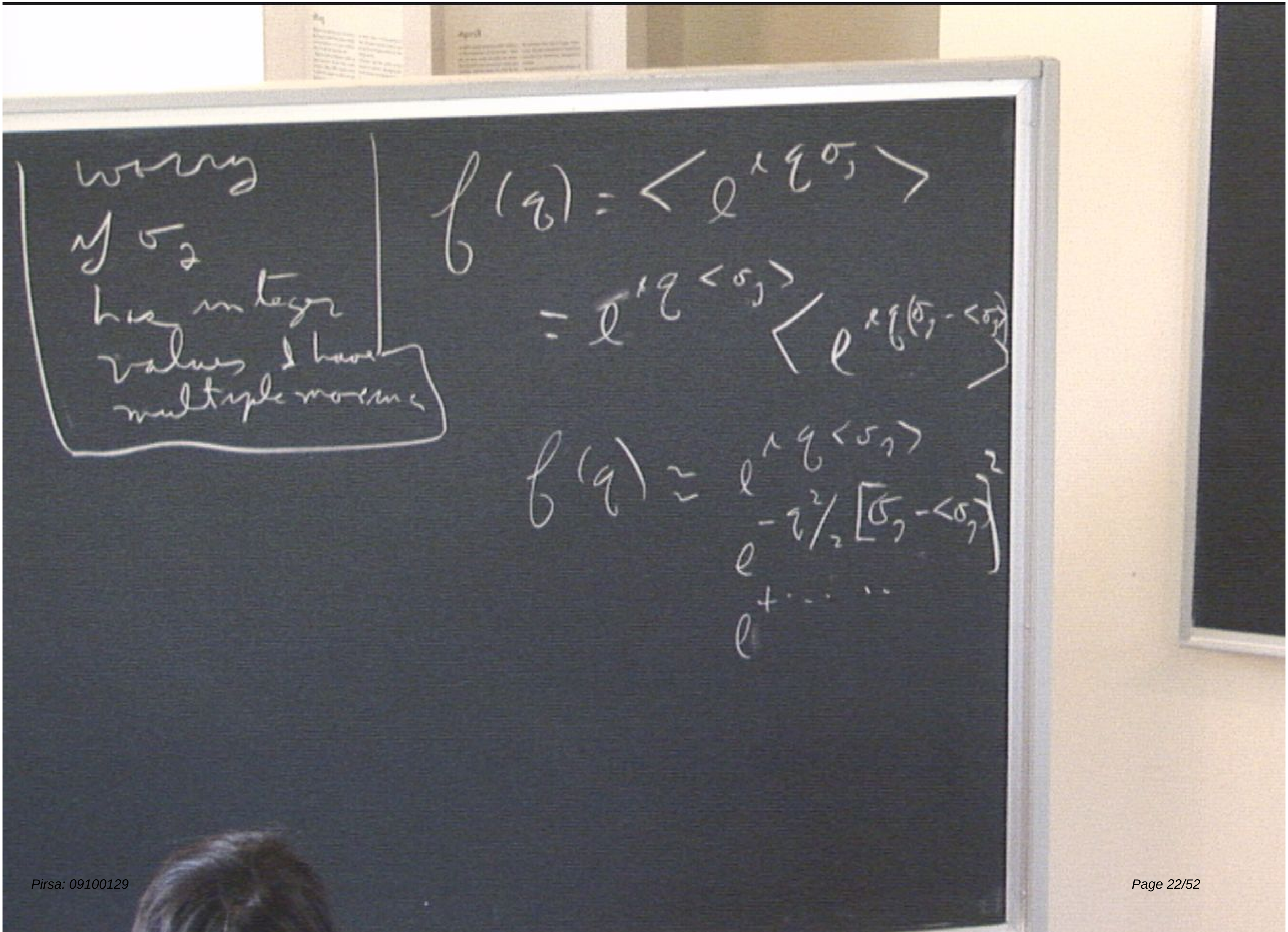
$$f(q) \simeq e^{iq\langle\sigma_z\rangle} e^{-q^2/_2 [\sigma_z - \langle\sigma_z\rangle]^2}$$



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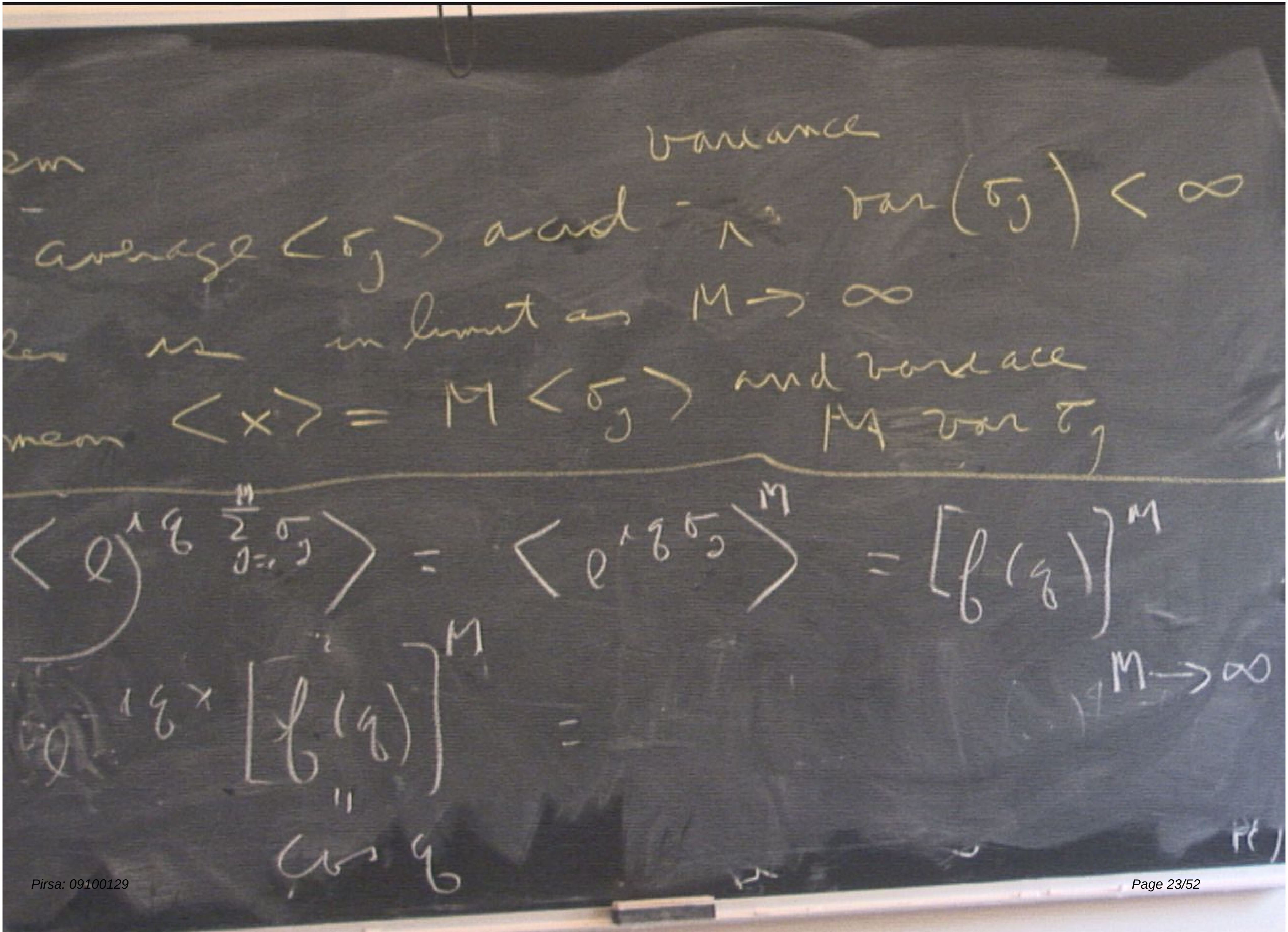


em

variance

average $\langle \sigma_j \rangle$ and $\mathrm{var}(\sigma_j) < \infty$

les in limit as $M \to \infty$

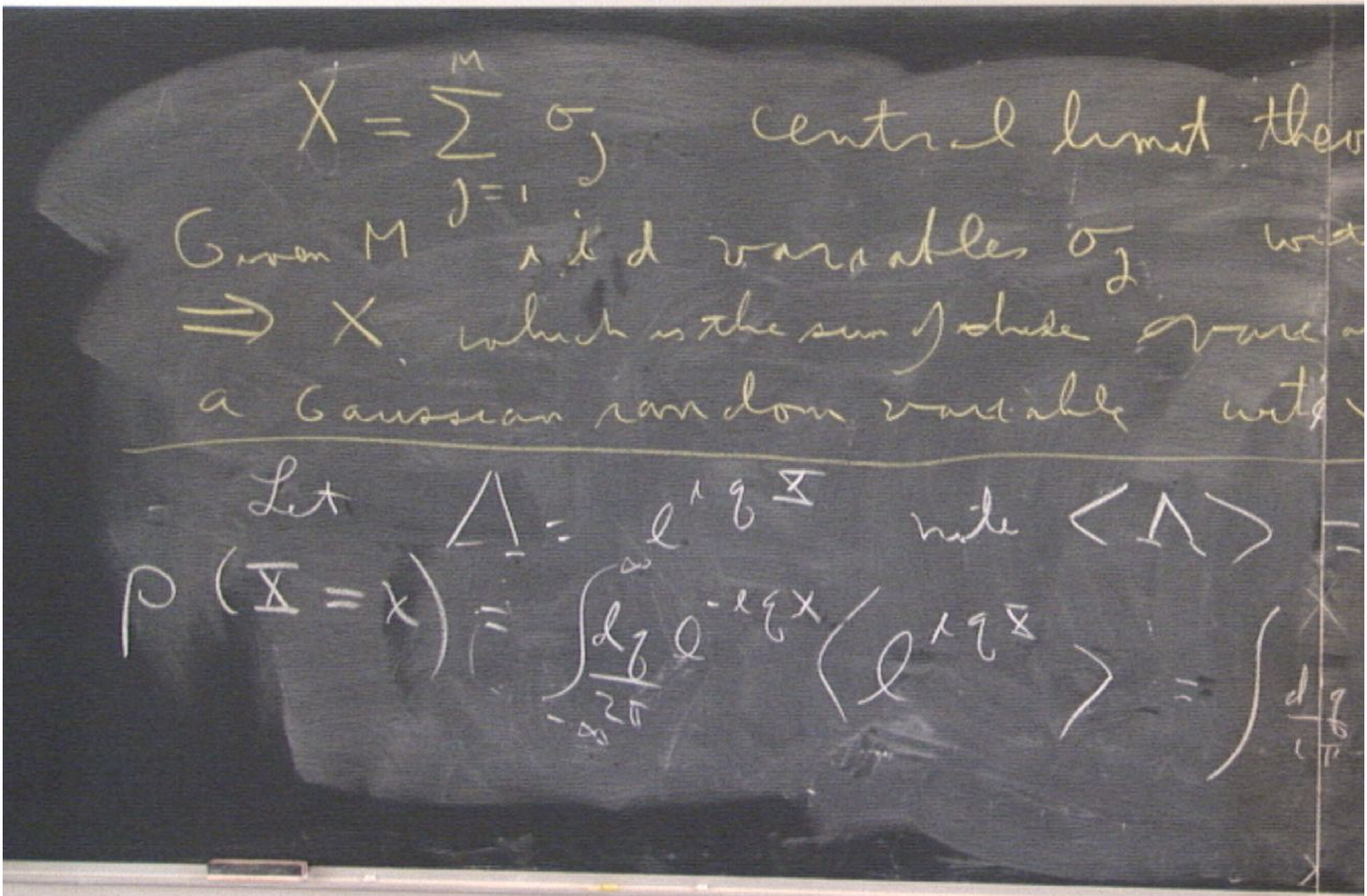
mean $\langle x \rangle = M \langle \sigma_j \rangle$ and variance $M \,\mathrm{var}\, \sigma_j$

$$\langle e^{i\xi \sum_{j=1}^{M} \sigma_j} \rangle = \langle e^{i\xi\sigma_j} \rangle^M = [f(\xi)]^M$$

$M \to \infty$

$$e^{i\xi x} \, [f(\xi)]^M =$$

$$f(\xi) = \cos \xi$$



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Given M i.i.d variables σ_j wit

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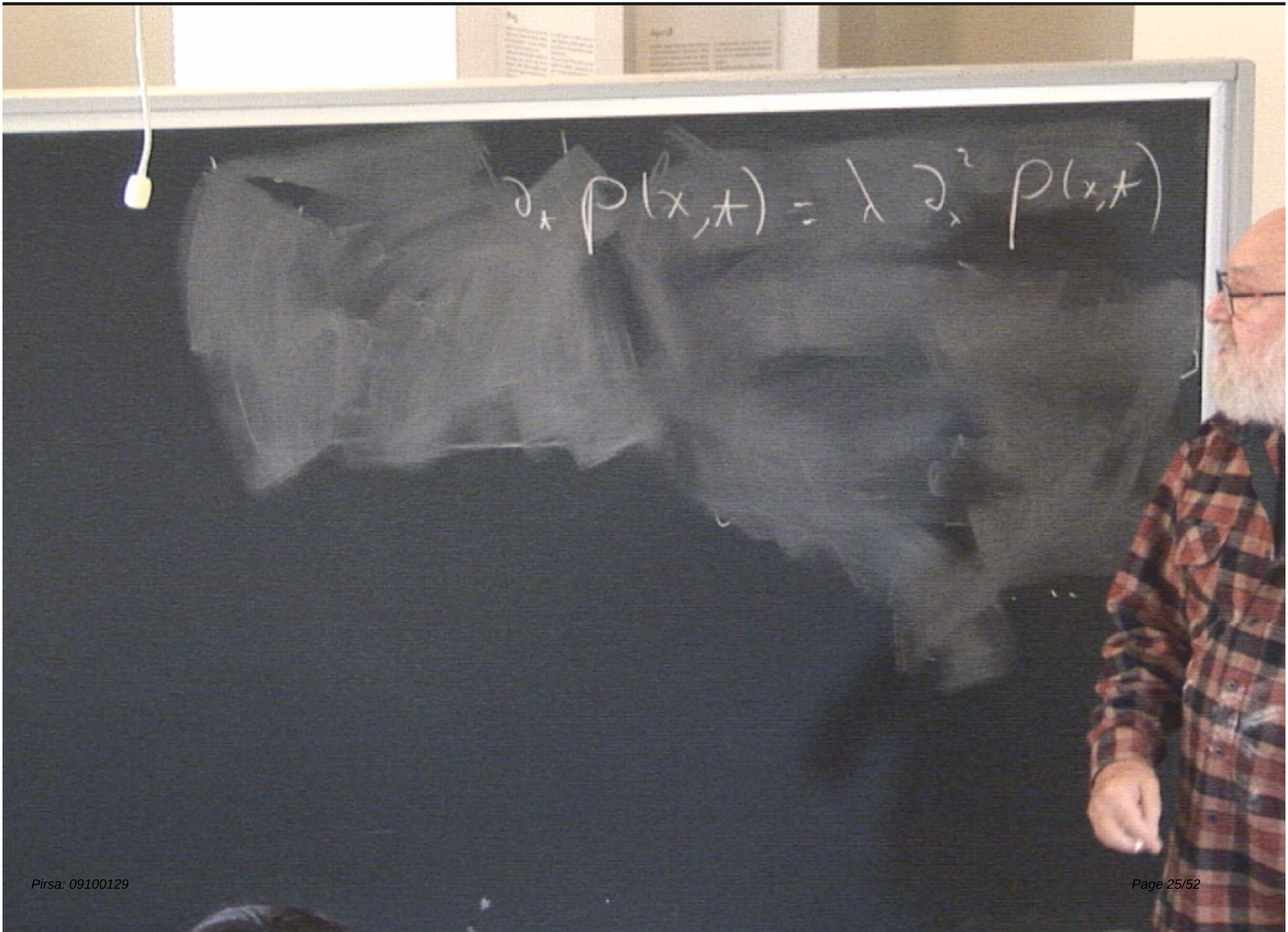
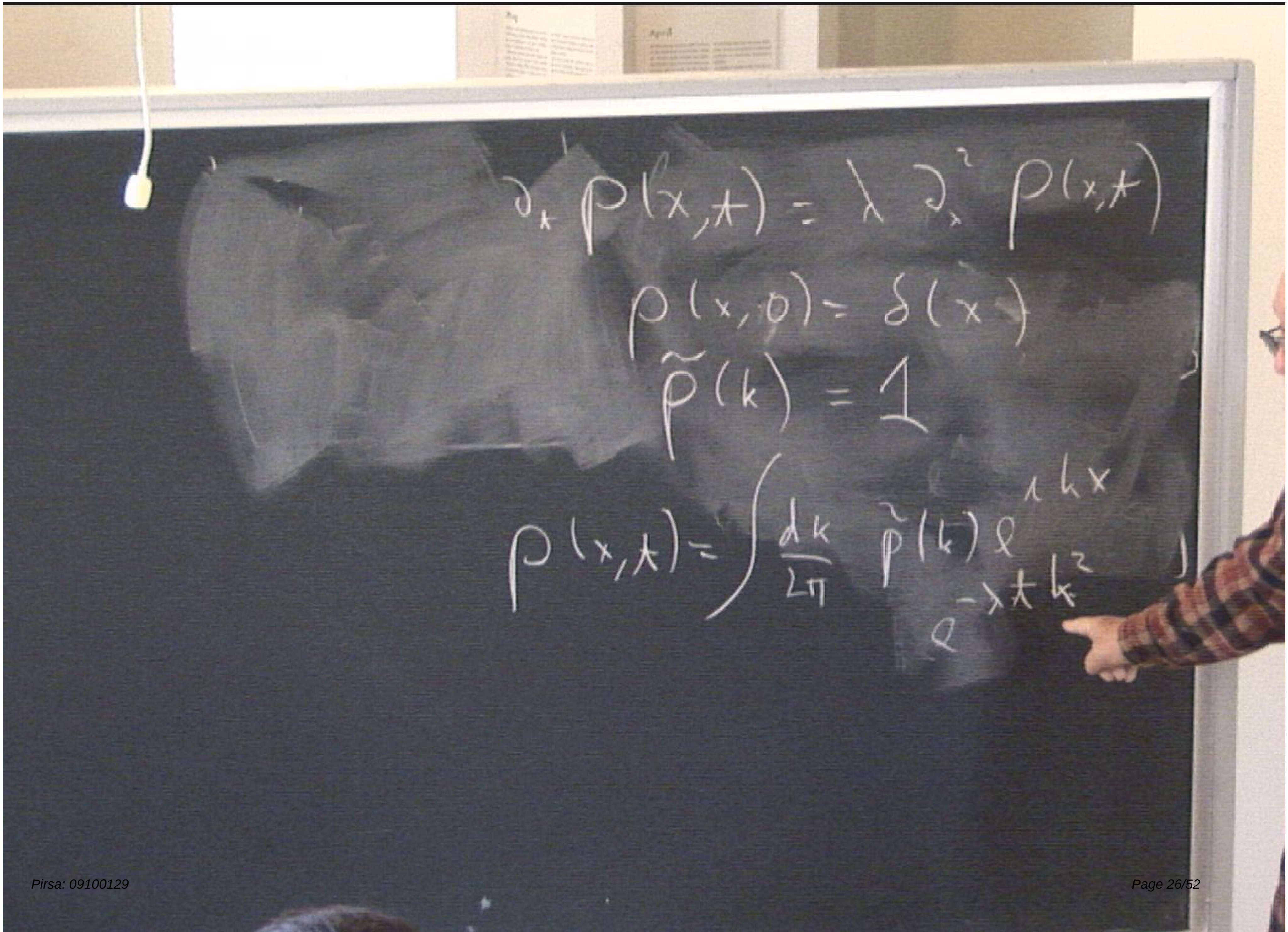
$$p(\mathbb{X} = x) = \int_{-\infty}^{\infty} \frac{dq}{2\pi} e^{-iqx} \langle e^{iq\mathbb{X}} \rangle = \int \frac{dq}{2\pi}$$



$$\partial_t \rho(x,t) = \lambda \partial_x^2 \rho(x,t)$$



$$\partial_t \rho(x,t) = \lambda \partial_x^2 \rho(x,t)$$

$$\rho(x,0) = \delta(x)$$

$$\tilde{\rho}(k) = 1$$

$$\rho(x,t) = \int \frac{dk}{2\pi} \tilde{\rho}(k) e^{ikx} e^{-\lambda t k^2}$$

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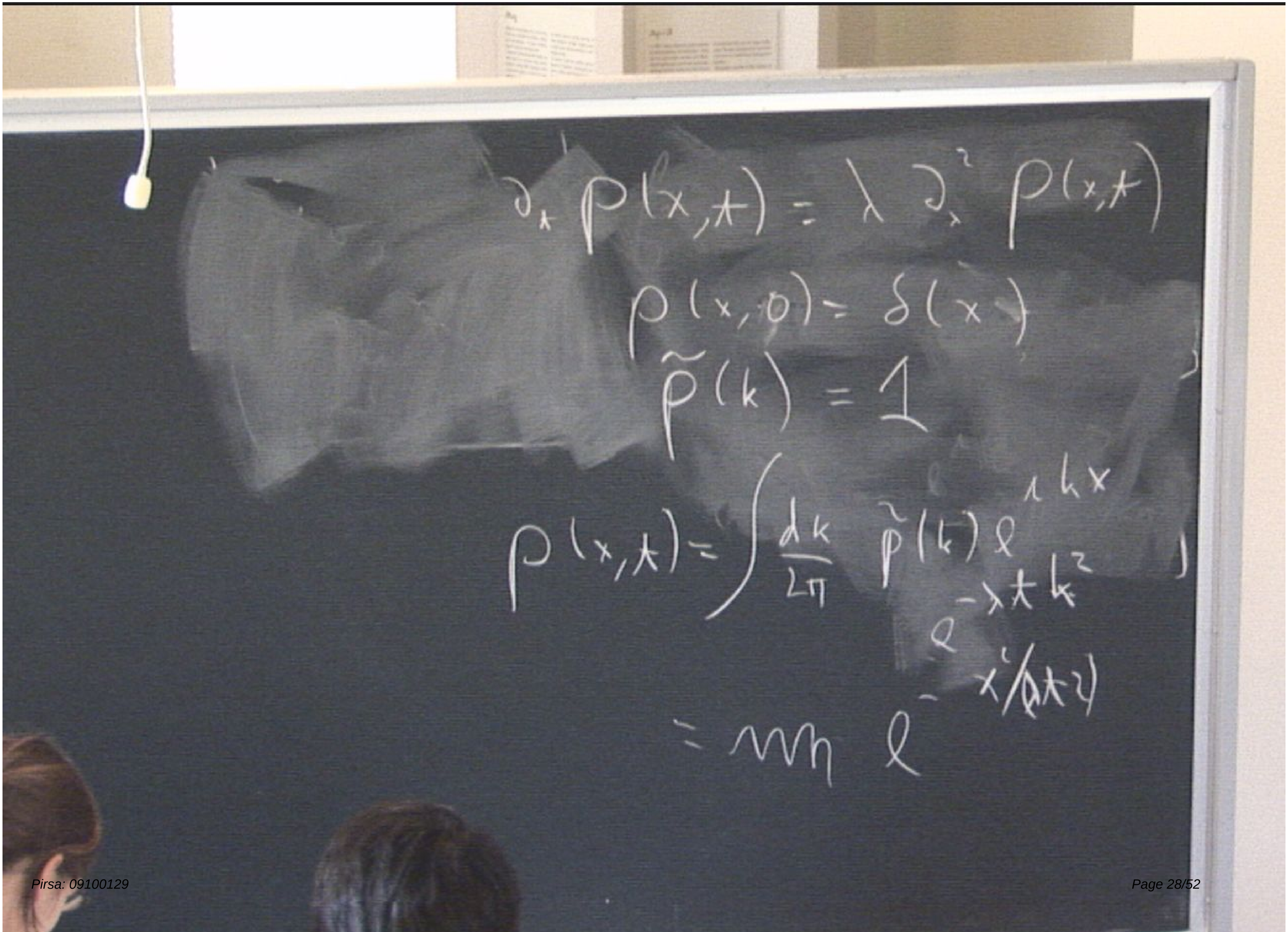
$$= \text{mn}\; e^{-x^2/(\lambda t 4)}$$



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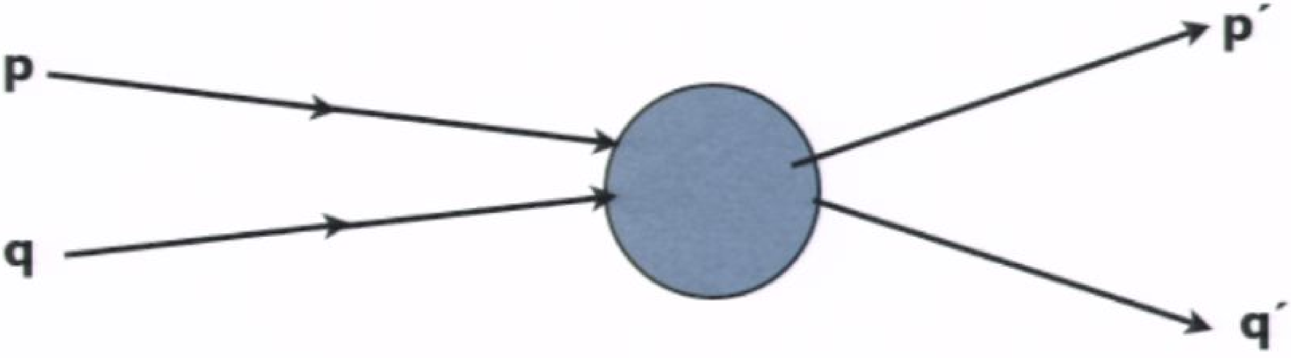
The scattering:



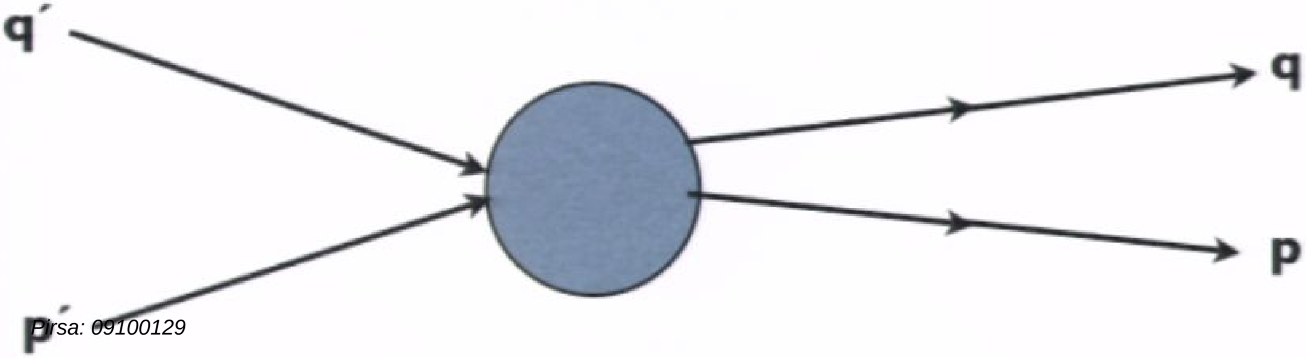
iven that there are particles available with the appropriate initial momentum, the scattering rate to a volume element of final momentum $d\mathbf{p}'\,d\mathbf{q}'$ can be written as $\mathbf{dp}'\,\mathbf{dq}'\ Q(\mathbf{p},\mathbf{q} \rightarrow \mathbf{p}',\mathbf{q}')$

he probability that we could get the particles we need for the scattering produce a factor

$f(\mathbf{p},\mathbf{r},t)\ \ \mathbf{dq}\ f(\mathbf{q},\mathbf{r},t)$, so that the total scattering rate for this process is

$$f(\mathbf{p},\mathbf{r},t) \int \mathbf{dq}\ f(\mathbf{q},\mathbf{r},t)\ \mathbf{dp}'\,\mathbf{dq}'\ Q(\mathbf{p},\mathbf{q} \rightarrow \mathbf{p}',\mathbf{q}')$$

The process itself *reduces* the number described by **p,r** at the rate shown. Conversely, there is an inverse process, and a corresponding rate of increase of $f(\mathbf{p},\mathbf{r},t)$

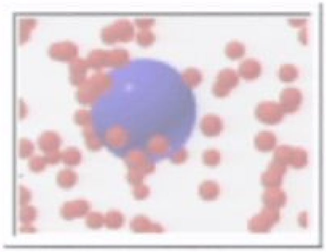


Outline: Momentum Hops and Time Dependence

- Brownian Motion
  - Define Situation
  - Calculate momentum
  - Calculate Variance
  - Calculate Probability Distribution
- Probability Distribution in Classical Mechanics
  - Statistical and Hamiltonian Dynamics
  - Probability Distributions in Dynamical Systems
  - time dependence of dynamical systems
    - calculation set up
    - calculation continued
    - calculation concluded
    - Poisson bracket
    - generalizing stat mech
    - time dependence in Hamiltonian systems
    - one-particle distribution
    - Classical Mechanics
- Brownian motion again: toward a unique solution
  - friction
  - collisions
    - calculation set up
    - calculation continued
    - calculation concluded
  - a unique probability distribution
  - Summary
- Boltzmann Equation
  - Scattering
    - forward
    - backward
    - all together
  - Symmetries
    - detailed balance-local equilibrium
    - conservation of particle number
    - H-theorem
    - sign of dissipation term
    - dS/dt
- Homework

Brownian motion:

Robert Brown (1773-1858) saw particles of pollen "dance around" in fluid under microscope. Thi motion was caused by many tiny particles hitting the grains of pollen.



The many moving tiny particles are of course **molecules of the liquid**. They were too small to see under a microscope when Brownian motion was discovered, but it was obvious they were there. You can see the molecules of liquid hitting the bigger particle in the animation on the left. (The size of the molecules has been dramatically *increased* in order to make them visible).

http://www.worsleyschool.net/science/files/brownian/motion.html

Albert Einstein (1905) explained this dancing by many, many collisions with molecules in fluid

$$dp/dt=......+\eta(t)-p/\tau$$

$p=(p_x, p_y, p_z)$ $\eta=(\eta_x, \eta_y, \eta_z)$ v.1

$\eta(t)$ is a Gaussian random variable resulting from random kicks produced by collisions. Since the kicks have random directions $<\eta(t)>=0$. Different collisions are assumed to be statistically independent

$<\eta_j(t)\ \eta_k(s)> =\Gamma\delta(t-s)\delta_{j,k}$ v.2

The relaxation time, τ, describes friction slowing down as the particles moves through the medium. In contrast Γ describes the extra momentum picked up via the collisions. Both represent the same physical effect, little particles hitting our big one. However, they operate in a somewhat different fashion. The individual kicks point in every which direction and only in the long run produce any concerted change in momentum. On the other hand the term in τ is a friction tending to continually push our particle toward smaller speeds relative to the

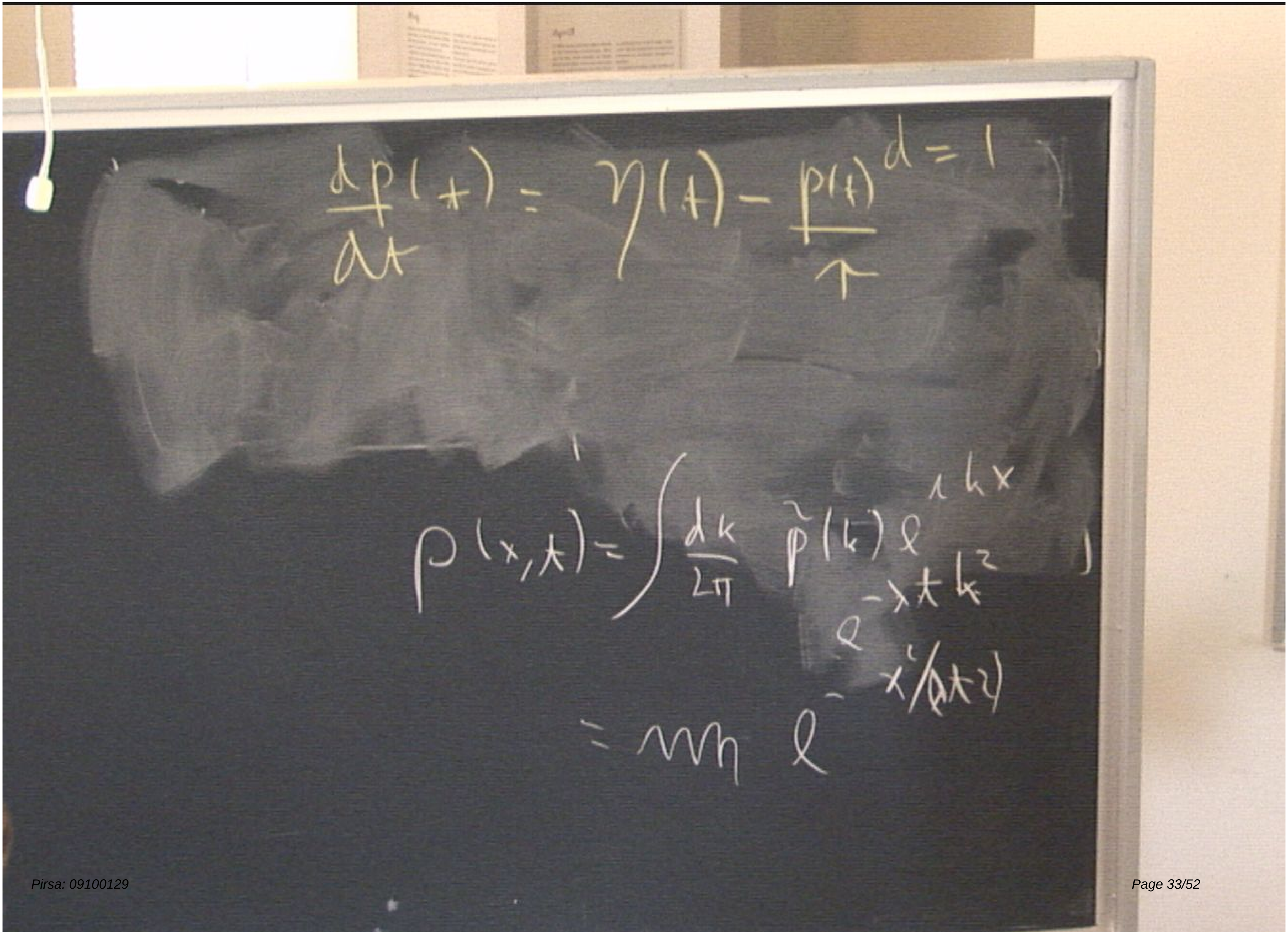
Calculate momentum from d**p**/dt=......+ $\eta(t)-p/\tau$

$$P(t) = \int_{-\infty}^{t} dt' \; \eta(t') \exp(-\frac{t-t'}{\tau}) \qquad \text{v.3}$$

Because *P(t)* is a sum of many random variables according to the central limit theorem, it must be a Gaussian random variable. Therefore it has a Gaussian probability distribution. In equilibrium, *P(t)* should have the variance, M kT, with M being the mass of the Brownian particle. In equilibrium it will have the Maxwell-Boltzmann probability distribution

$$\rho(\mathbf{p}) = (\frac{\beta}{2\pi M})^{3/2} \exp[-\beta p^2/(2M)]$$

Notice that if this works out for us, it will be our first "proof" that the ideas of Gibbs, Boltzmann, and Maxwell about the canonical distribution was correct. So we would have a proof that this "law" works, at least in this situation. In physics, we often use laws long before there is any substantial proof that they are correct. We use little bits of evidence, intuition, and guesswork and gradually convince ourselves that X "must be" right. If X is attractive, we hold on to that view until there is overwhelming evidence to the contrary.



$$\frac{d\rho(t)}{dt} = \eta(t) - \frac{\rho(t)}{\tau} \qquad d=1$$

$$\rho(x,t) = \int \frac{dk}{2\pi}\, \tilde{\rho}(k)\, e^{ikx}\, e^{-\lambda t k^2}$$

$$= \; e^{-x^2/(\lambda t 4)}$$

Calculate momentum from $d\mathbf{p}/dt = \ldots\ldots + \eta(t) - p/\tau$

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Calculate Variance of P(t)

$$< p_j(t)p_k(s) >= \int_{-\infty}^{t} du \int_{-\infty}^{s} dv < \eta_j(t)\eta_k(s) >$$

v.4

$$< p_j(t)p_k(s) >= \int_{-\infty}^{t} du \int_{-\infty}^{s} dv \Gamma \delta_{j,k} \delta(u - v) \exp[-(t - u) / \tau - (s - v) / \tau]$$

.... if $t > s$ the integral over u always gets a contribution from the delta-function so that this expression then becomes

$$< p_j(t)p_k(s) >= \int_{-\infty}^{s} dv \, \Gamma \delta_{j,k} \exp[-(t + s - 2v) / \tau]$$

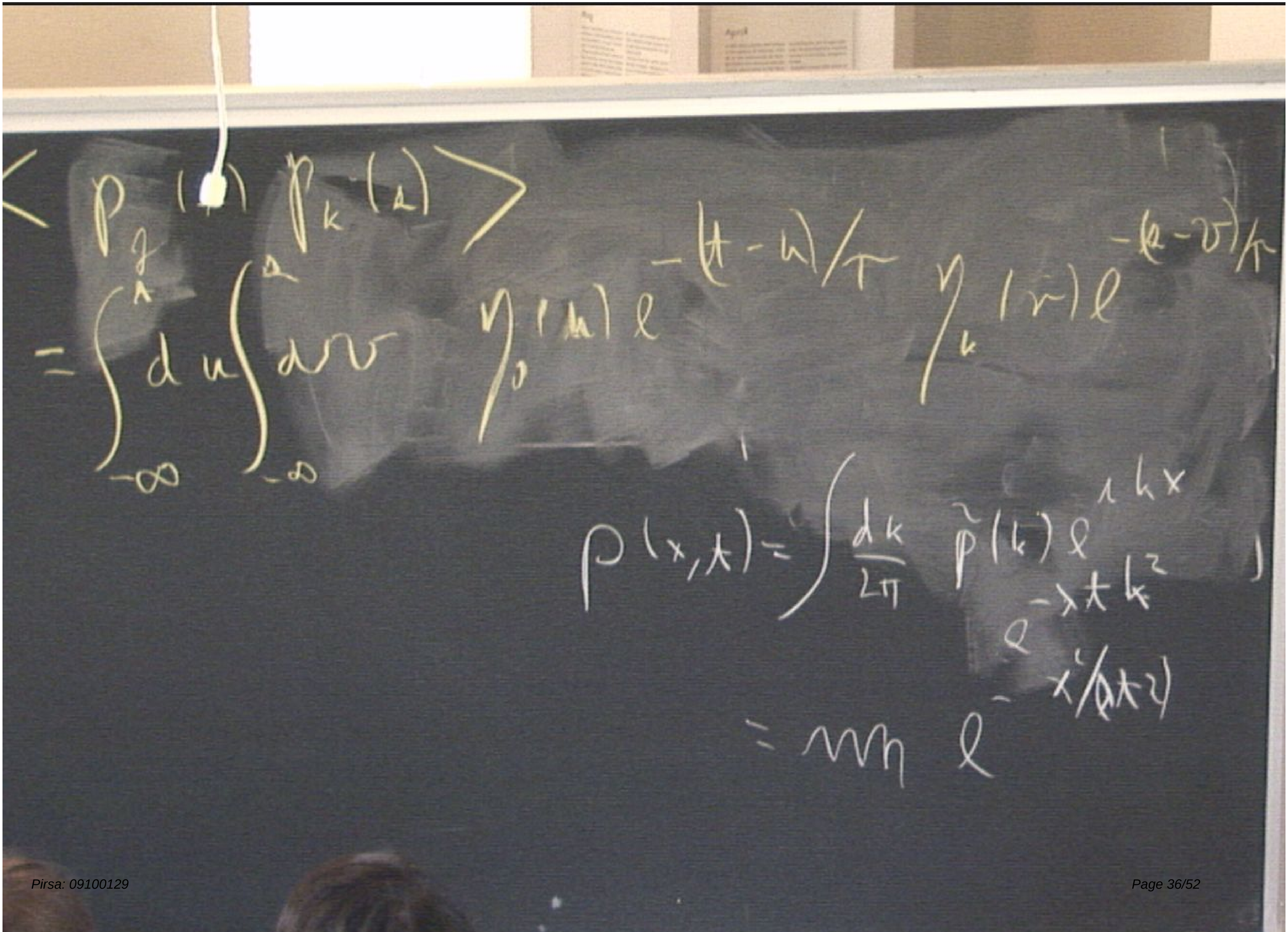
v.5

$$= \frac{\delta_{j,k}}{2} \Gamma \tau \exp[- | t - s | / \tau]$$

so we see that $p_j^2/(2M)$, where M is the mass of the Brownian particle is on one hand given by

$$< \frac{p_j^{\;2}}{2M} >= \Gamma \tau \; / \; (4M)$$

On the other hand, we know that in classical physics this quantity is kT/2. Thus we obtain th relation between the two parameters in the Einstein model.



$$\langle \rho_q(t)\, \rho_k(s) \rangle$$

$$= \int_{-\infty}^{t} du \int_{-\infty}^{s} dv \; \eta_q(u)\, e^{-(t-u)/\tau}\, \eta_k(v)\, e^{-(s-v)/\tau}$$

$$\rho(x,t) = \int \frac{dk}{2\pi}\, \tilde{\rho}(k)\, e^{ikx}\, e^{-\lambda t k^2}$$

$$= \text{mn}\; e^{-x^2/(\lambda t 2)}$$

Calculate momentum from $d\mathbf{p}/dt = \ldots\ldots + \eta(t) - p/\tau$

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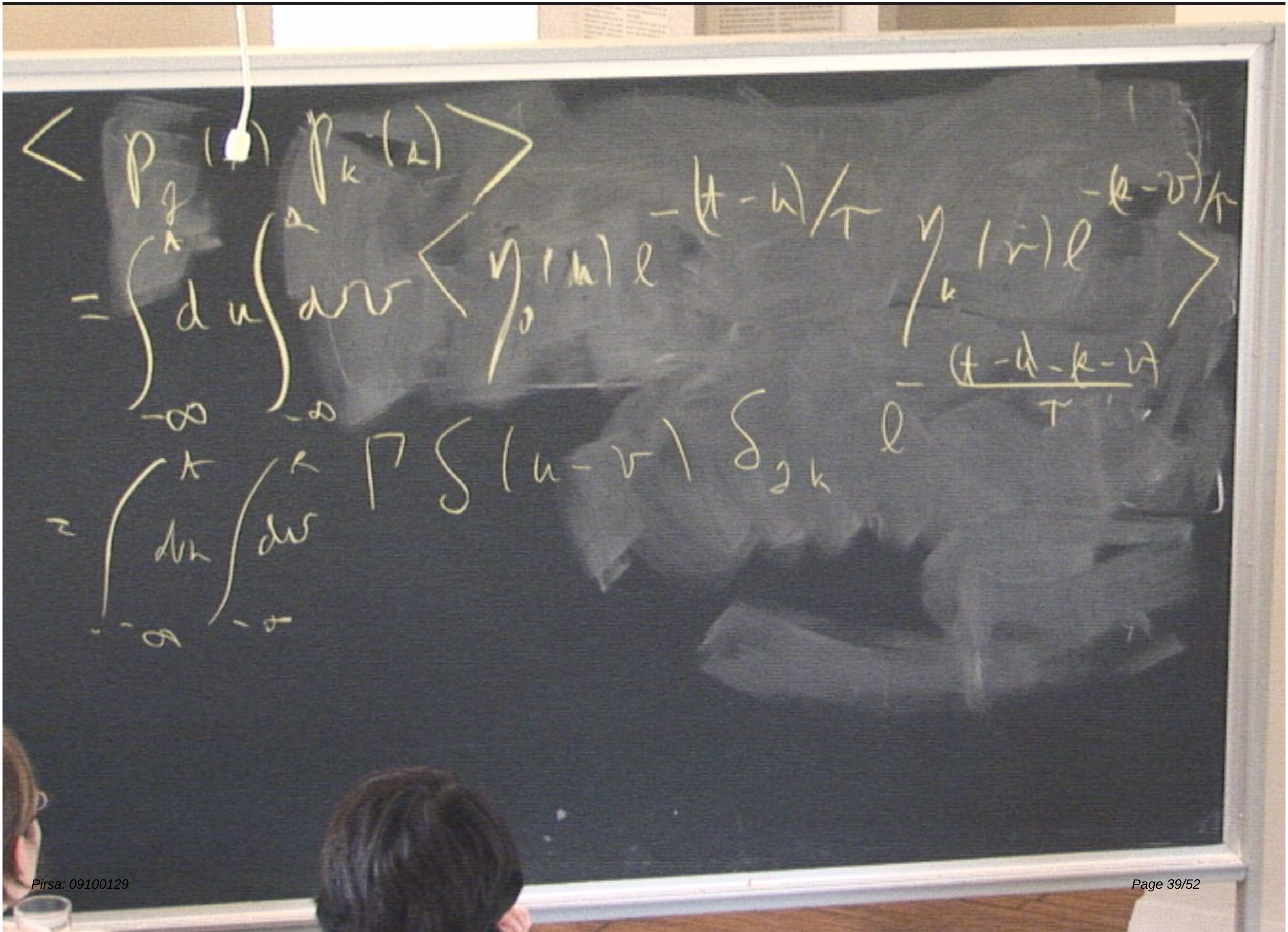
$$\left\langle p_j(t)\, p_k(s) \right\rangle$$

$$= \int_{-\infty}^{t} du \int_{-\infty}^{s} dv \left\langle \eta_j(u)\, e^{-(t-u)/\tau}\, \eta_k(v)\, e^{-(s-v)/\tau} \right\rangle$$

$$= \int dv$$



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$$= \int_{-\infty}^{t} du \int_{-\infty}^{s} dv\ \Gamma\, \delta(u-v)\, \delta_{jk}\, e^{-\frac{(t-u-s-v)}{\tau}}$$

Calculate Variance of P(t)

$$< p_j(t)p_k(s) >= \int_{-\infty}^{t} du \int_{-\infty}^{s} dv < \eta_j(t)\eta_k(s) >$$

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On the other hand, we know that in classical physics this quantity is kT/2. Thus we obtain th relation between the two parameters in the Einstein model.

Probability distribution

$\Gamma\tau = 2MkT$

Whenever this relation is satisfied, p has the right variance, MkT, and the right Maxwell-Boltzmann probability distribution.

$$\rho(\mathbf{p}) = (\frac{\beta}{2\pi M})^{3/2} \exp[-\beta p^2/(2M)]$$

More generally, if we have a Hamiltonian, $H(\boldsymbol{p},\boldsymbol{r})$, for the one-particle system, the Maxwell-Boltzmann distribution takes the form

$\rho(\boldsymbol{p},\boldsymbol{r}) = exp[-\beta H(\boldsymbol{p},\boldsymbol{r})]/Z$, v.7

where, the the simplest case the Hamiltonian is

$H(\boldsymbol{p},\boldsymbol{r}) = p^2/(2M) + U(\boldsymbol{r})$

Maxwell and Boltzmann expected that, in appropriate circumstances, if they waited long enough, a Hamiltonian system would get to equilibrium and they would end up with a Maxwell-Boltzmann probability distribution

Question: Should we not be able to derive this distribution from classical mechanics alone? Maybe we should have to assume that we must long enough to reach equilibrium? Anything more?

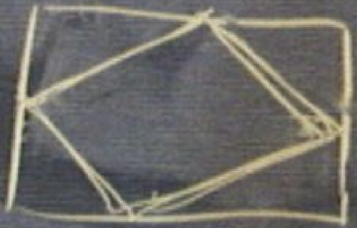
Something of the form v.7 is called by mathematicians a Gibbs measure and by physicists a Boltzmann distribution or often a Maxwell-Boltzmann distribution. Why? Should we care?

$$(t)\,\eta_k(s)\rangle$$

$$= \int_{-\infty}^{t} du \int_{-\infty}^{s} dv \left\langle \eta_j(u)\, e^{-(t-u)/\tau}\, \eta_k(v)\, e^{-(s-v)/\tau} \right\rangle$$

$$e^{-\frac{(t-u-s-v)}{\tau}}$$

$$\int_{-\infty}^{t} du \int_{-\infty}^{s} dv \; \Gamma\, \delta(u-v)\, \delta_{jk}$$



Statistical and Hamiltonian Dynamics

We have that the equilibrium ρ=exp(−βH)/Z. How can this arise from time dependence c system? One very important possible time-dependence is given by Hamiltonian mechanics

$$\frac{dq_\alpha}{dt} = \frac{\partial \mathcal{H}}{\partial p_\alpha}$$

$$\frac{dp_\alpha}{dt} = -\frac{\partial \mathcal{H}}{\partial q_\alpha}$$

The simplest case is a particle moving in a potential field with a Hamiltonian

$$\mathcal{H} = \mathbf{p}^2/(2M) + U(\mathbf{r})$$

and consequently equations of motion

$$\frac{d\mathbf{p}}{dt} = -\nabla U$$

$$\frac{d\mathbf{r}}{dt} = \mathbf{p}/M$$

The statistical mechanics of such situations is given by a probability density function ρ(**p**,**r**,t) such that the probability of finding the particle in a volume element **dp dr** about **p**,**r** at time t is ρ(**p**,**r**,t) **dp dr**. The next question is, what is the time-dependence of this probability density? Or maybe, how do we get equilibrium

Time Dependence of Dynamical systems:
A much more general problem

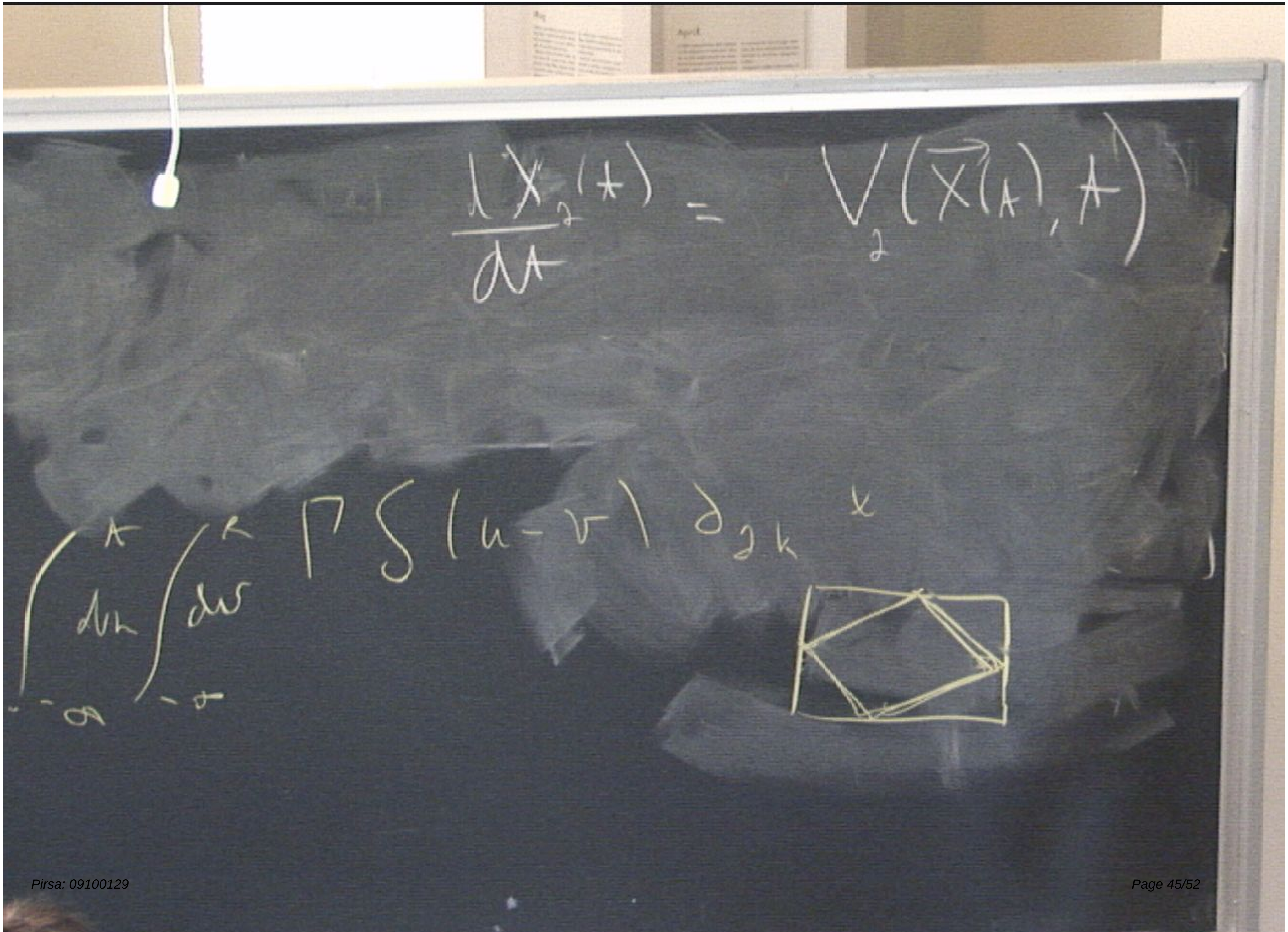
Instead of carrying around the variables **p** and **r**, let me do something with much simpler formulas. I'm going to imagine solving the dynamical systems problem in which there is a differential equation $dX/dt=V(X(t),t)$ to get a solution $X(t)$. I will have a probability function $\rho(x,t)\,dx$ which is the probability that the solution will be in the interval dx about x. This is a probability because, when we start out the initial data is not just one value of x but a probability distribution, given by $\rho(x,0)$. So the situation at a later time must be described by a probability distribution then as well. So what is the time dependence of the probability distribution? One way to approach this problem is to ask what does the distribution mean. Specifically, if we have some function $g(X)$ of the particle coordinates at time t, that function has an average at time t given by $\int dx\; g(x)\; \rho(x,t)$. Naturally the average at time t + dt is $\int dx\; g(x)\; \rho(x,t+dt)$. That same average is obtained by taking the solution at time t+dt, which is

$$X(t+dt) \approx X(t)+V(X(t),t))dt \qquad \text{v.7}$$

and calculate its average using the probability distribution which is appropriate at the earlier time, i.e. the average is $\int dx\; g(x+dt\,V(x,t))\; \rho(x,t)$. Equate those two expressions for the average

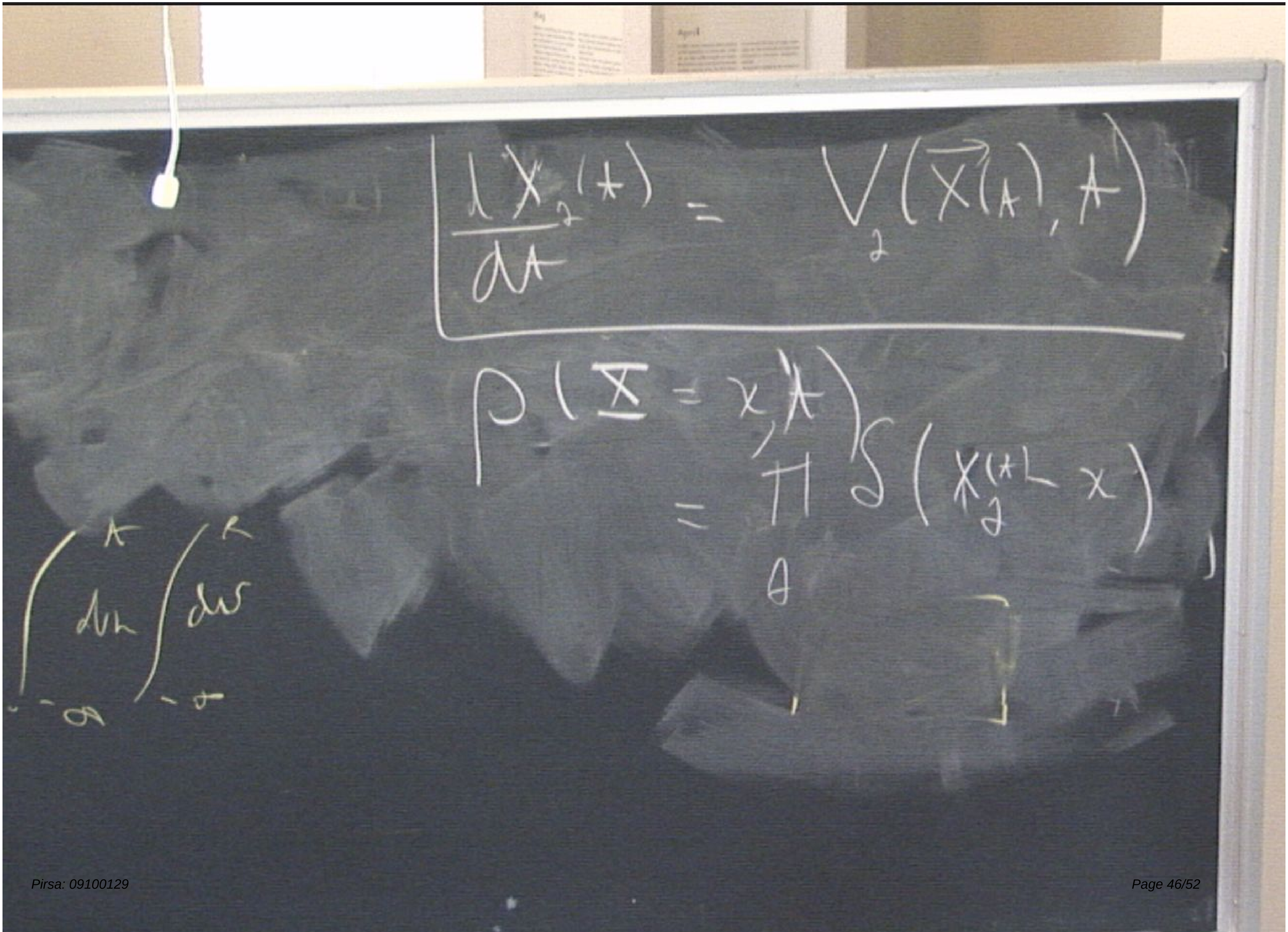
$$\int dx\; g(x)\; \rho(x,t+dt) \;=\int dx\; g(x+dt\,V(x,t))\; \rho(x,t) \qquad \text{v.8}$$

carry this result forward



$$\frac{dX_2(t)}{dt} = V_2(\vec{X}(t), t)$$

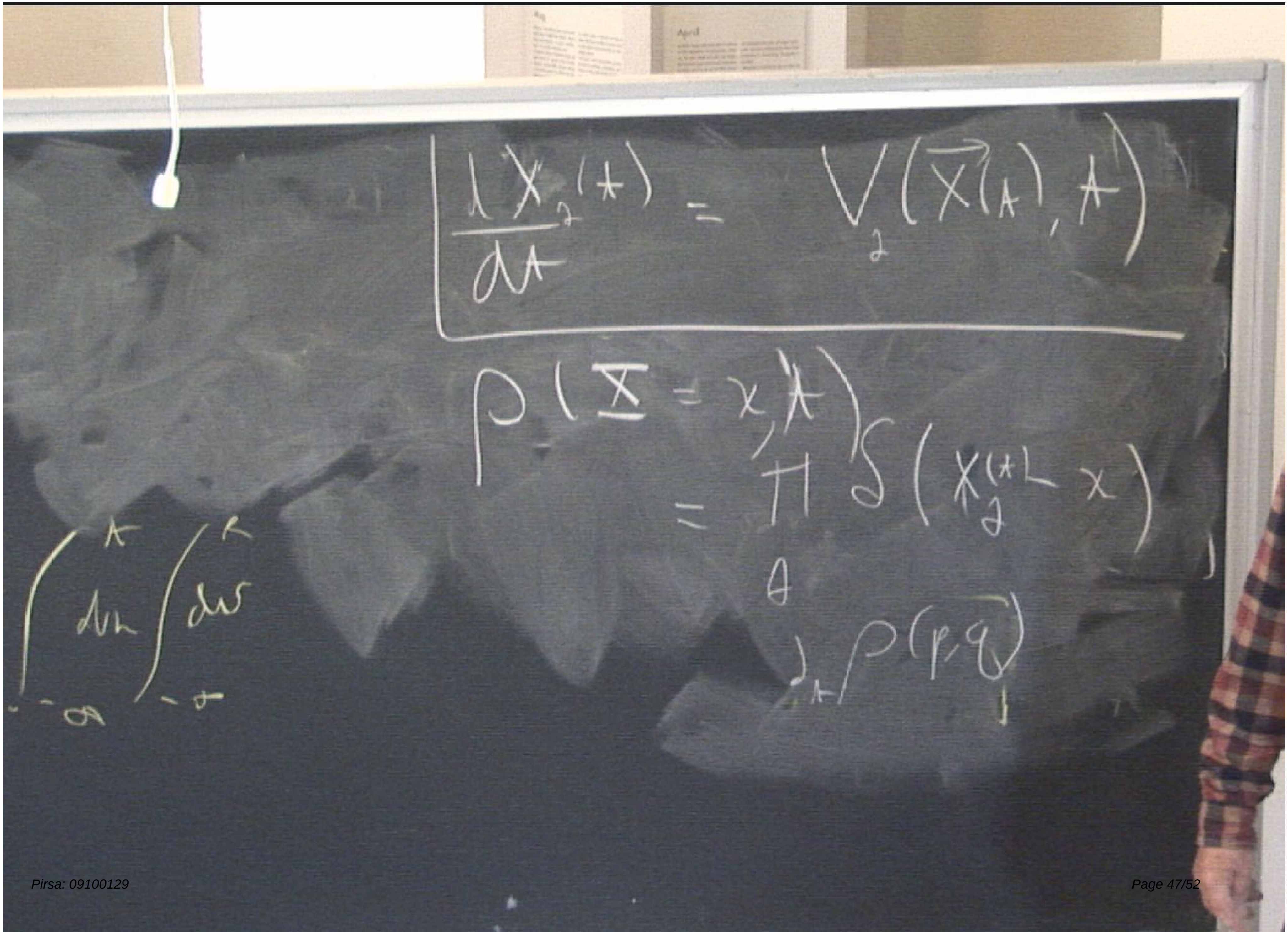
$$\int_{-\infty}^{t} du \int_{-\infty}^{t} dv \, \Gamma \delta(u-v) \, \partial_{2k} \quad x$$



$$\boxed{\frac{dX_2(t)}{dt} = V_2(\vec{X}(t), t)}$$

$$\rho(X = x, t) = \prod_a \delta(X_a(t) - x)$$

$$\int_{-\infty}^{t} dr \int_{-\infty}^{r} ds$$

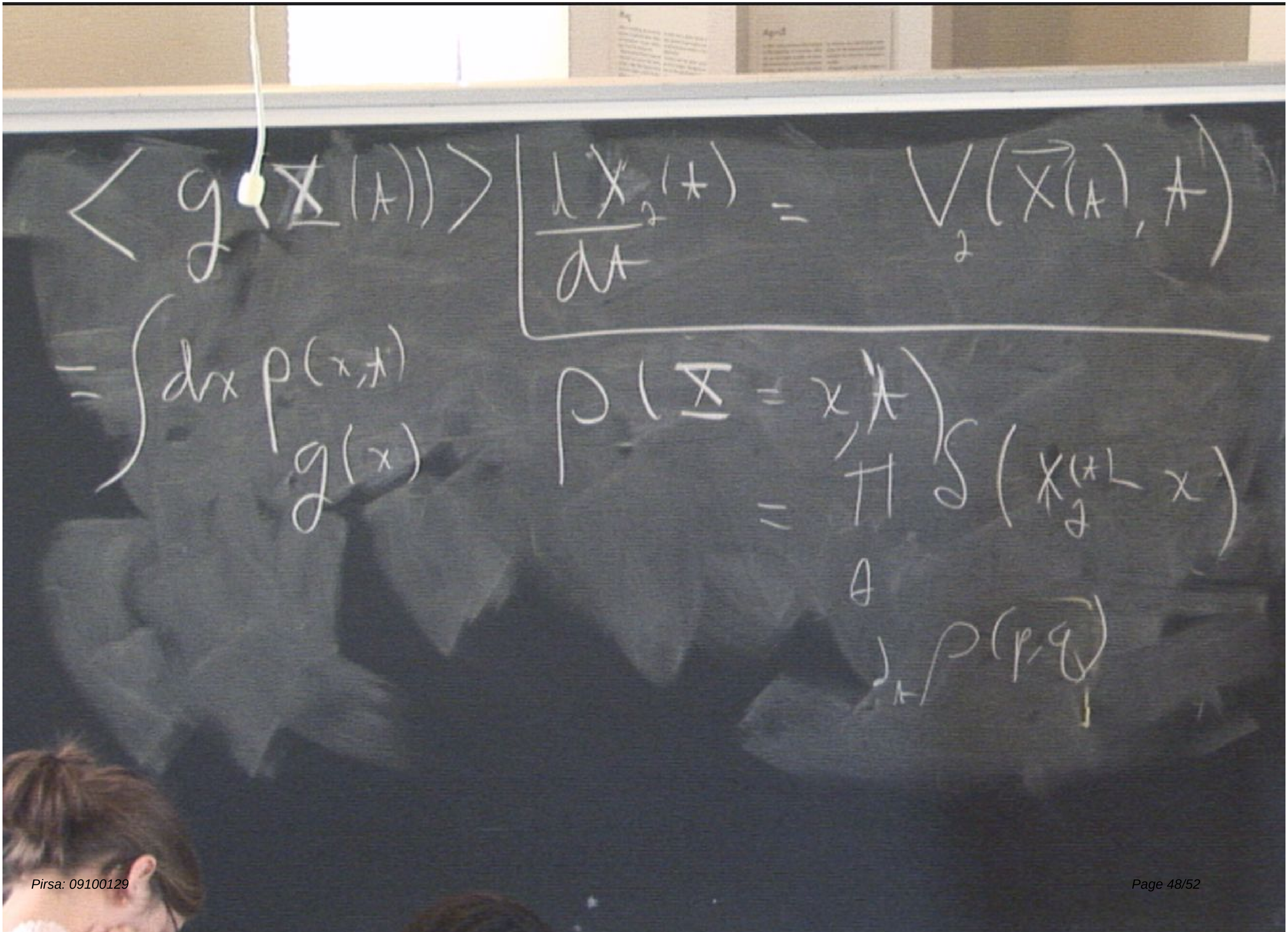


$$\boxed{\frac{dX_a(t)}{dt} = V_a(\vec{X}(t), t)}$$

$$\rho(\underline{X} = x, t) = \prod_a \delta(X_a(t) - x)$$

$$d_t \rho(p,q)$$

$$\int_{-\infty}^{t} dt \int_{-\infty}^{t} dt'$$



$$\langle g(\underline{X}(t))\rangle$$

$$= \int dx\, \rho(x,t)\, g(x)$$

$$\boxed{\frac{dX_2(t)}{dt} = V_2(\vec{X}(t), t)}$$

$$\rho(\underline{X} = x, t) = \prod_a \delta(X_a(t) - x)$$

$$d_t \rho(p,q)$$

Time Dependence of Dynamical systems: A much more general problem

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$$\int dx\, g(x)\, \rho(x,t+dt) = \int dx\, g(x+dt\, V(x,t))\, \rho(x,t) \qquad \text{v.8}$$

carry this result forward

Calculation Continued .....

$$\int dx\, g(x)\, \rho(x,t+dt) = \int dx\, g(x+dt\, V(x,t))\, \rho(x,t)$$

expand to first order in dt

$$\int dx\, g(x)\, \rho(x,t) + dt \int dx\, g(x)\partial_t\rho(x,t) = \int dx\, g(x)\, \rho(x,t) + \int dx\, dt\, V(x,t)[d_x g(x)]\, \rho(x,t)$$

throw away the things that cancel against each other to get

$$\int dx\, g(x)\partial_t\rho(x,t) - \int dx\, V(x,t)[\partial_x g(x)]\, \rho(x,t) = 0$$

integrate by parts on the right hand side, using the fact that ρ(x,t) vanishes at x=± infinity

$$\int dx\, g(x)\{\partial_t\rho(x,t) + \partial_x [V(x,t)\, \rho(x,t)]\}=0$$

Notice that *g(x)* is arbitrary. If this left hand side is going to always to vanish, the { } must vanish. We then conclude that $\partial_t\rho(x,t) + \partial_x [V(x,t)\, \rho(x,t)] = 0$. That's for one coordinate,
If there are lots of coordinates this equation reads

$$\partial_t\rho(x,t) + \rho(x,t)\sum_j(\partial_{x_j}V_j) + \sum_j V_j\partial_{x_j}\rho(x,t) = 0$$ v.9

We call the second term on the left the divergence term. It describes the dilation of the volume element by the changes in the *x*'s caused by the time development. The last term is the direct result of the time-change in each coordinate *X(t)* Now we have the general result for the time development of the probability density. We go look at the Hamiltonian

$$\langle g(X(t))\rangle = \int dx\, \rho(x,t)\, g(x)$$

$$\boxed{\frac{dX_2(t)}{dt} = V_2(\vec{X}(t), t)}$$

$$\partial_t g(X(t)) = \partial_x g(X)\, V(X(t), t)$$

$$\theta$$

$$= \cancel{2x}\, x^2$$

$$\partial_t \rho(p,q)$$

$$\partial_t g(x) = 0$$

Calculation Continued .....

$$\int dx\; g(x)\; \rho(x,t+dt) \;=\int dx\; g(x+dt\,V(x,t))\; \rho(x,t)$$

expand to first order in dt

$$\int dx\; g(x)\; \rho(x,t) + dt \int dx\; g(x)\partial_t\rho(x,t) \;= \int dx\; g(x)\; \rho(x,t) + \int dx\; dt\,V(x,t)[d_x g(x)]\; \rho(x,t)$$

throw away the things that cancel against each other to get

$$\int dx\; g(x)\partial_t\rho(x,t) \;-\; \int dx\,V(x,t)[\partial_x g(x)]\; \rho(x,t) =0$$

integrate by parts on the right hand side, using the fact that $\rho(x,t)$ vanishes at x=± infinity

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Notice that *g(x)* is arbitrary. If this left hand side is going to always to vanish, the { } must vanish. We then conclude that $\partial_t\rho(x,t) + \partial_x\,[V(x,t)\;\rho(x,t)] =0$. That's for one coordinate, If there are lots of coordinates this equation reads

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