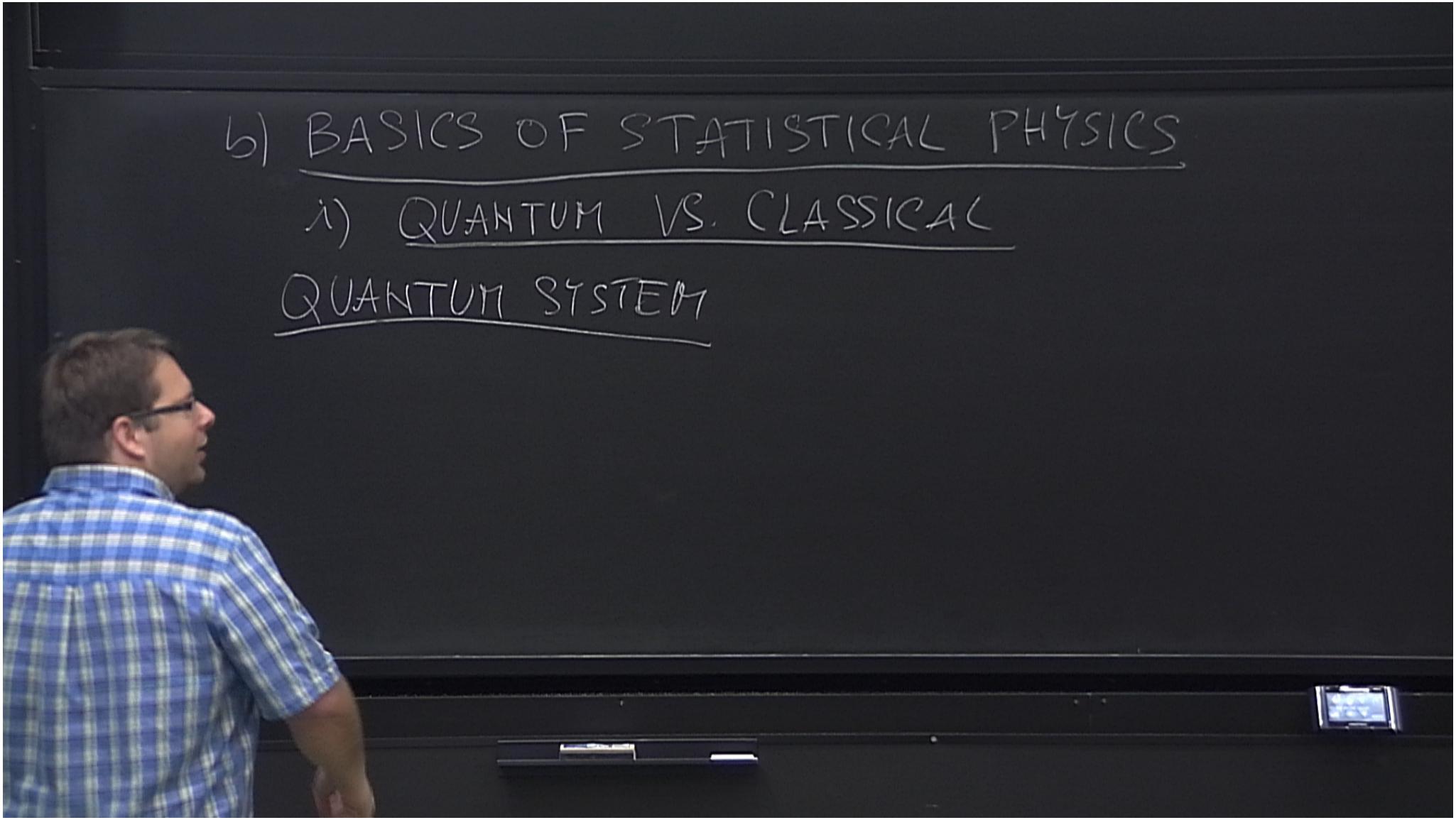
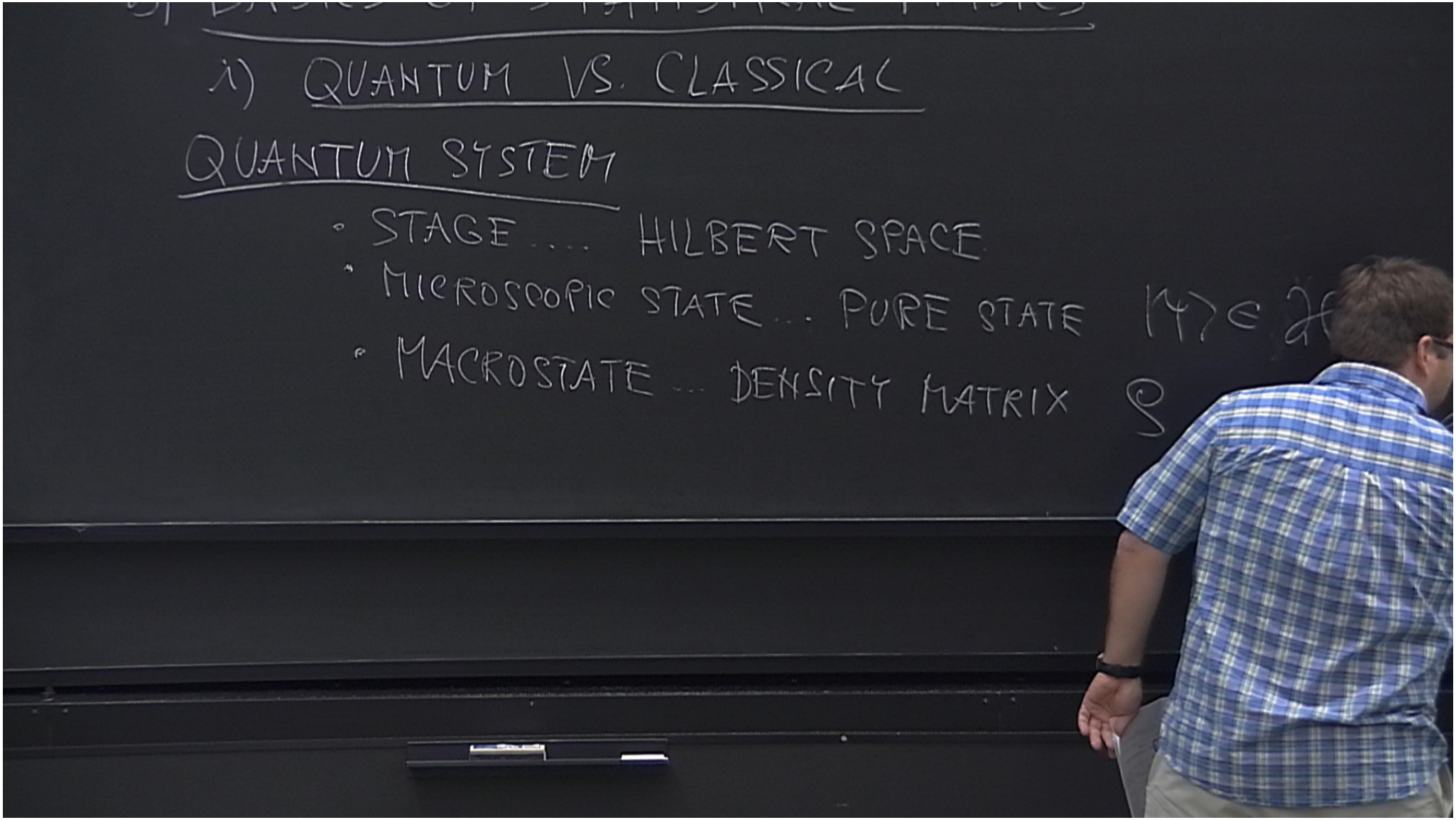
Title: PSI 2016/2017 Statistical Mechanics - Lecture 2

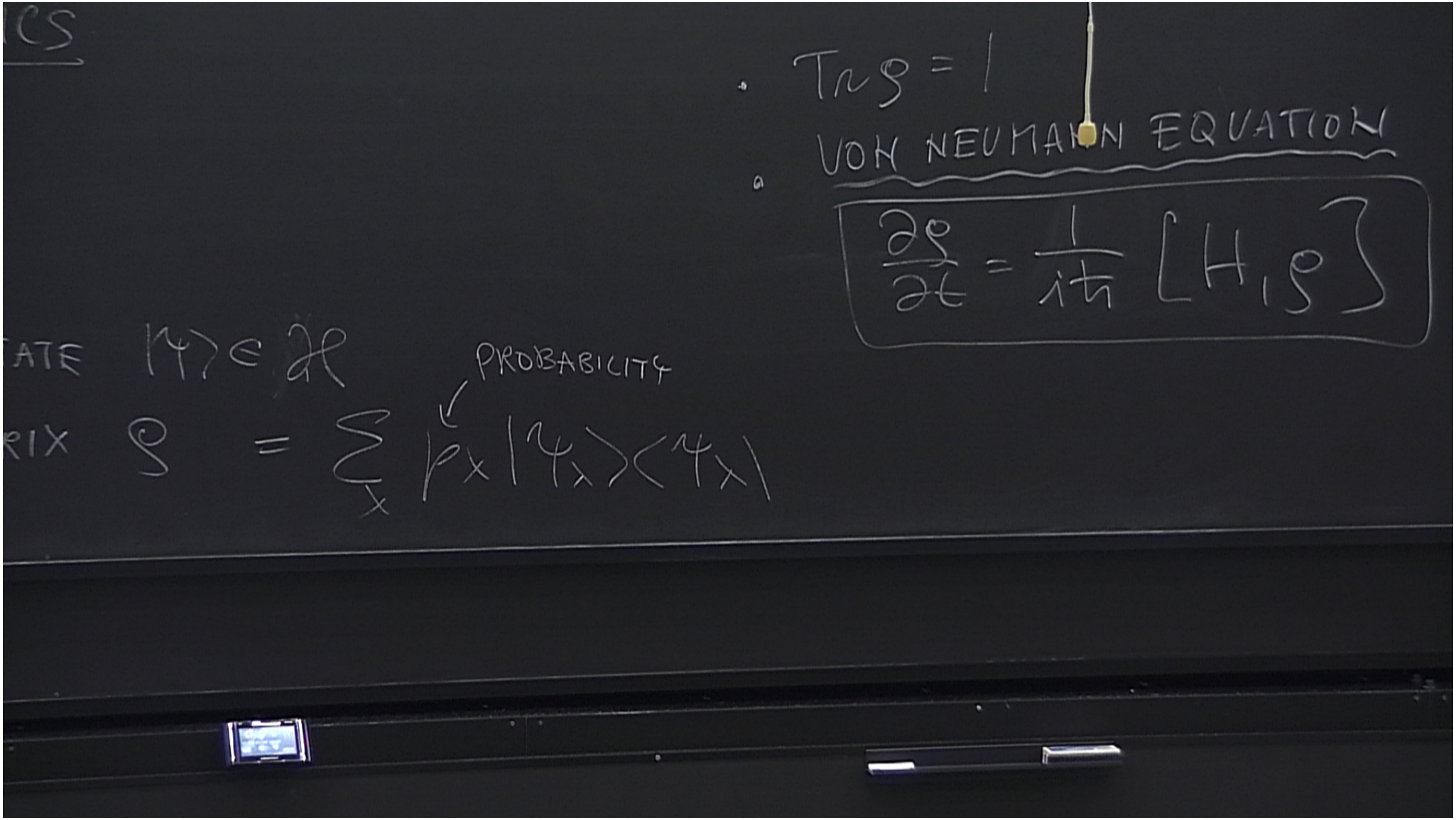
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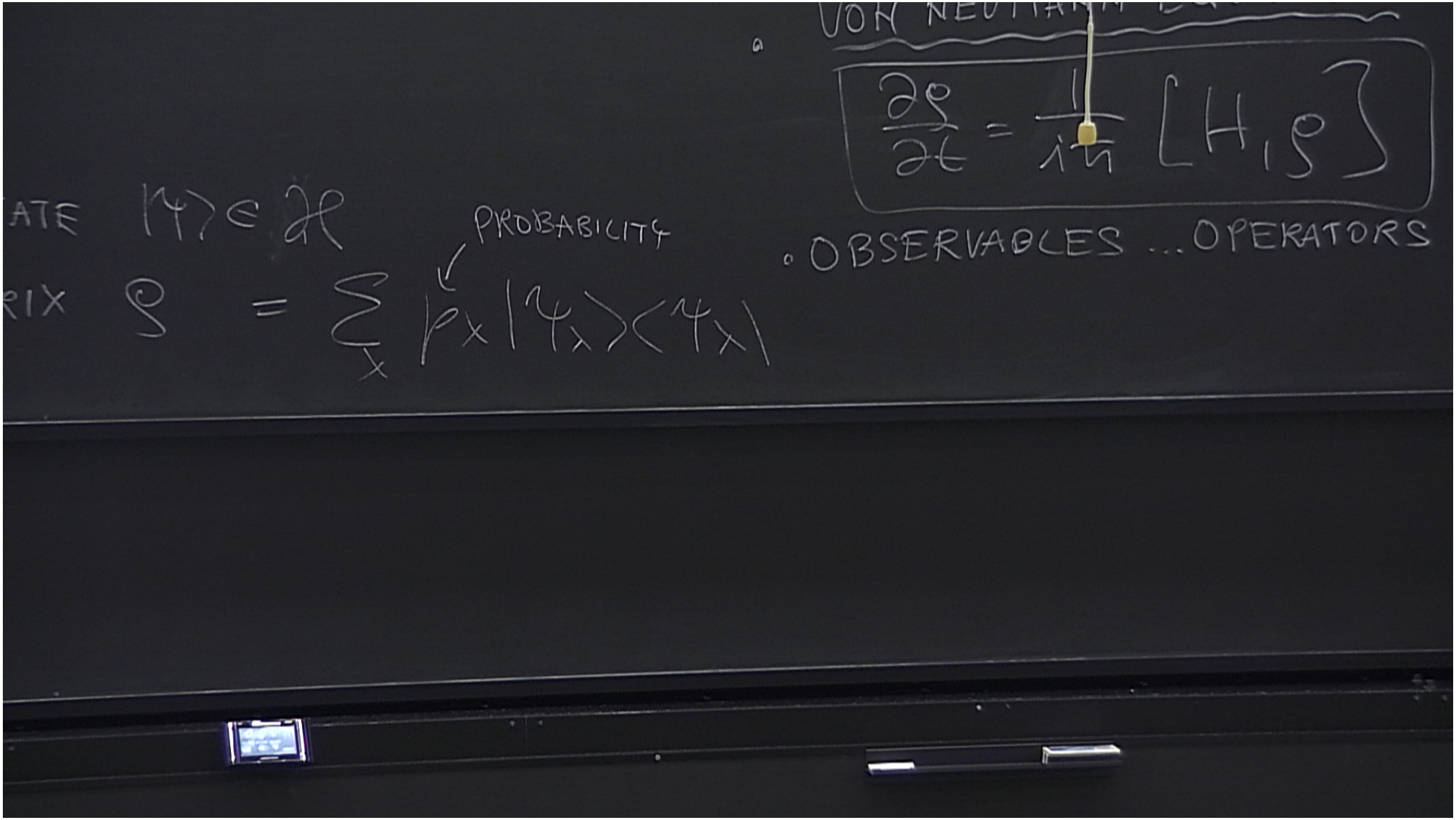
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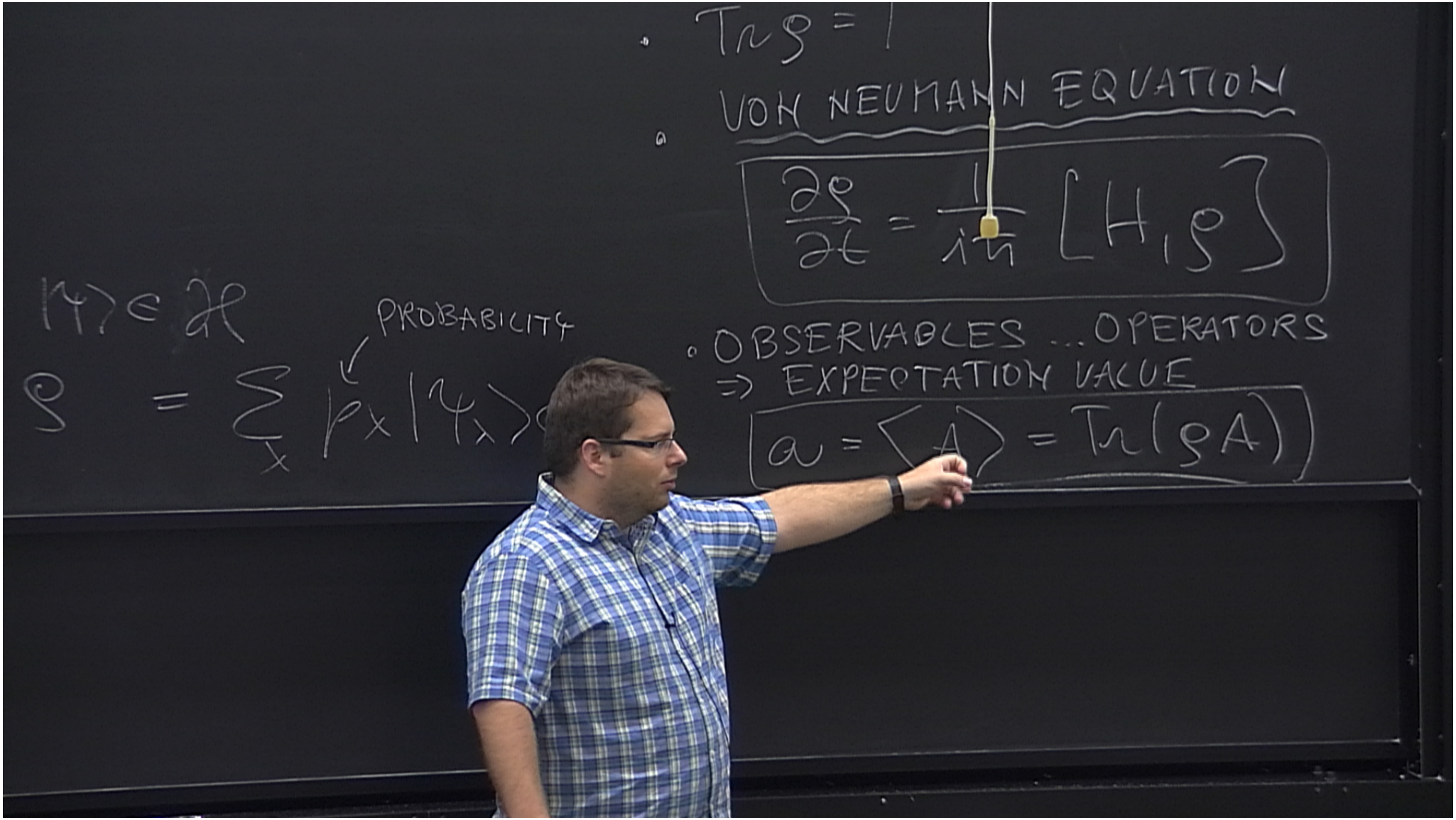
Abstract:

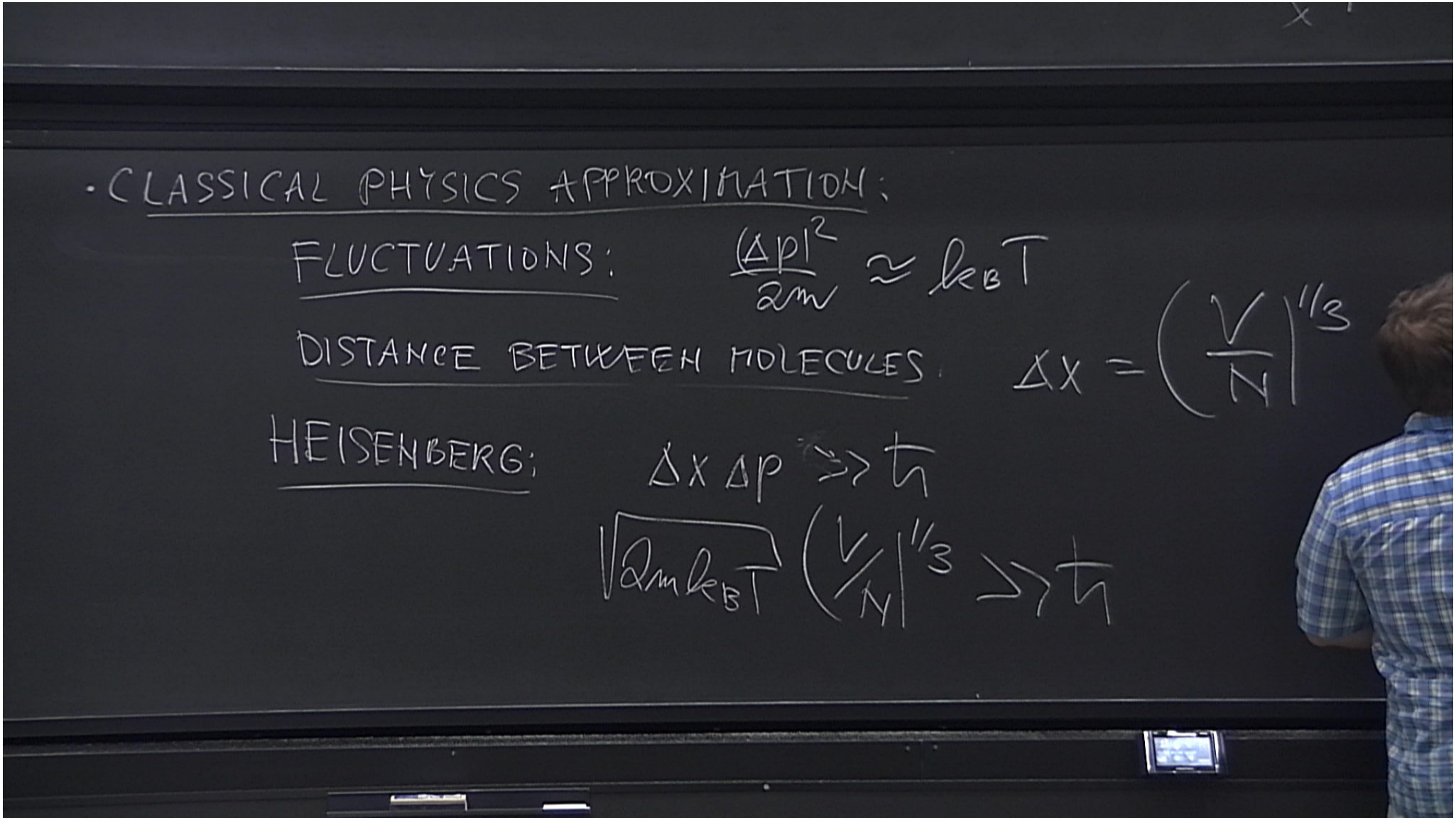

b) BASICS OF STATISTICAL PHYSICS
i) QUANTUM VS. CLASSICAL
QUANTUM SYSTEM

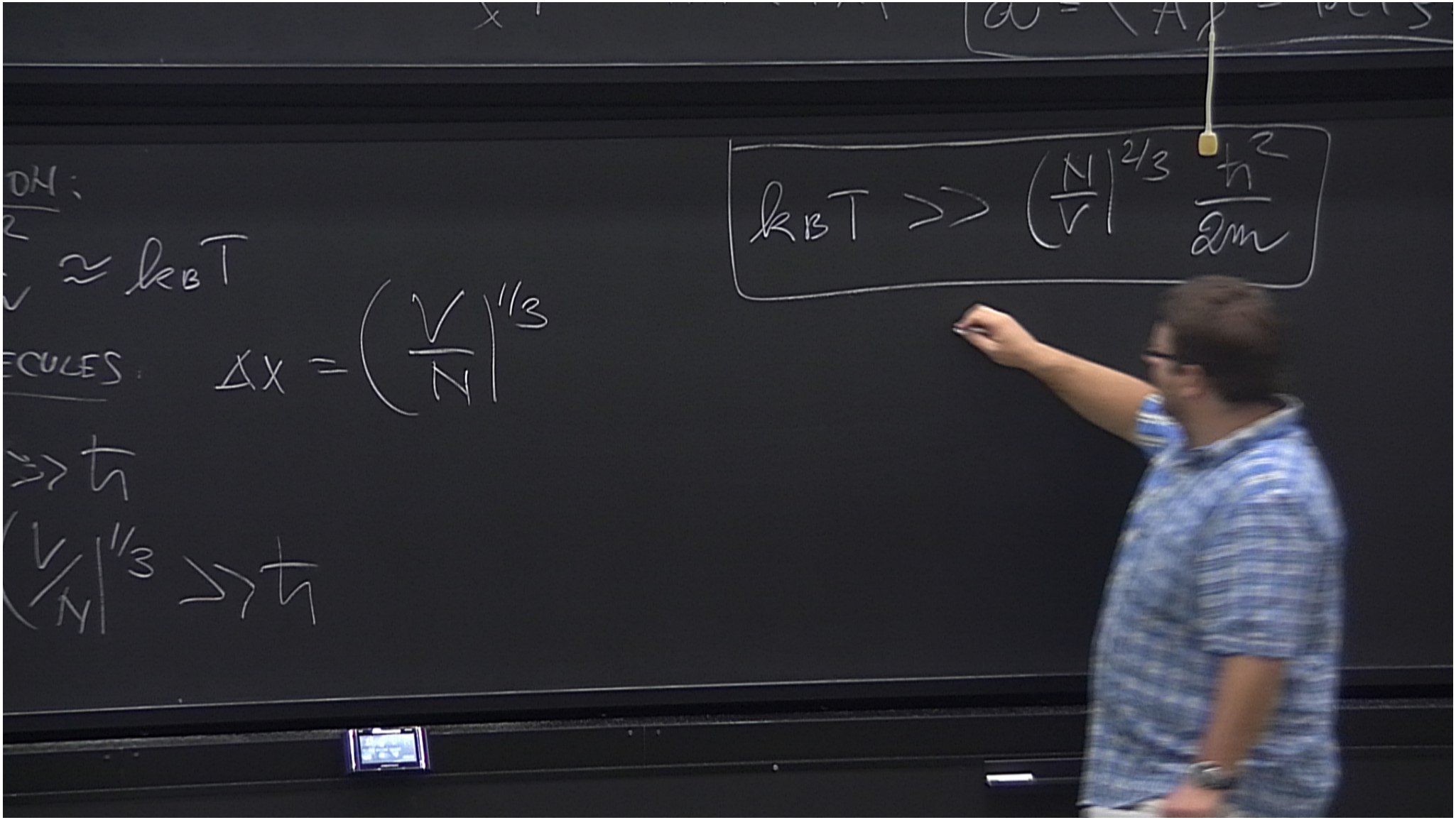

1) QUANTUM VS. CLASSICAL
QUANTUM SYSTEM
• STAGE ... HILBERT SPACE
• MICROSCOPIC STATE ... PURE STATE
• MACROSTATE ... DENSITY MATRIX

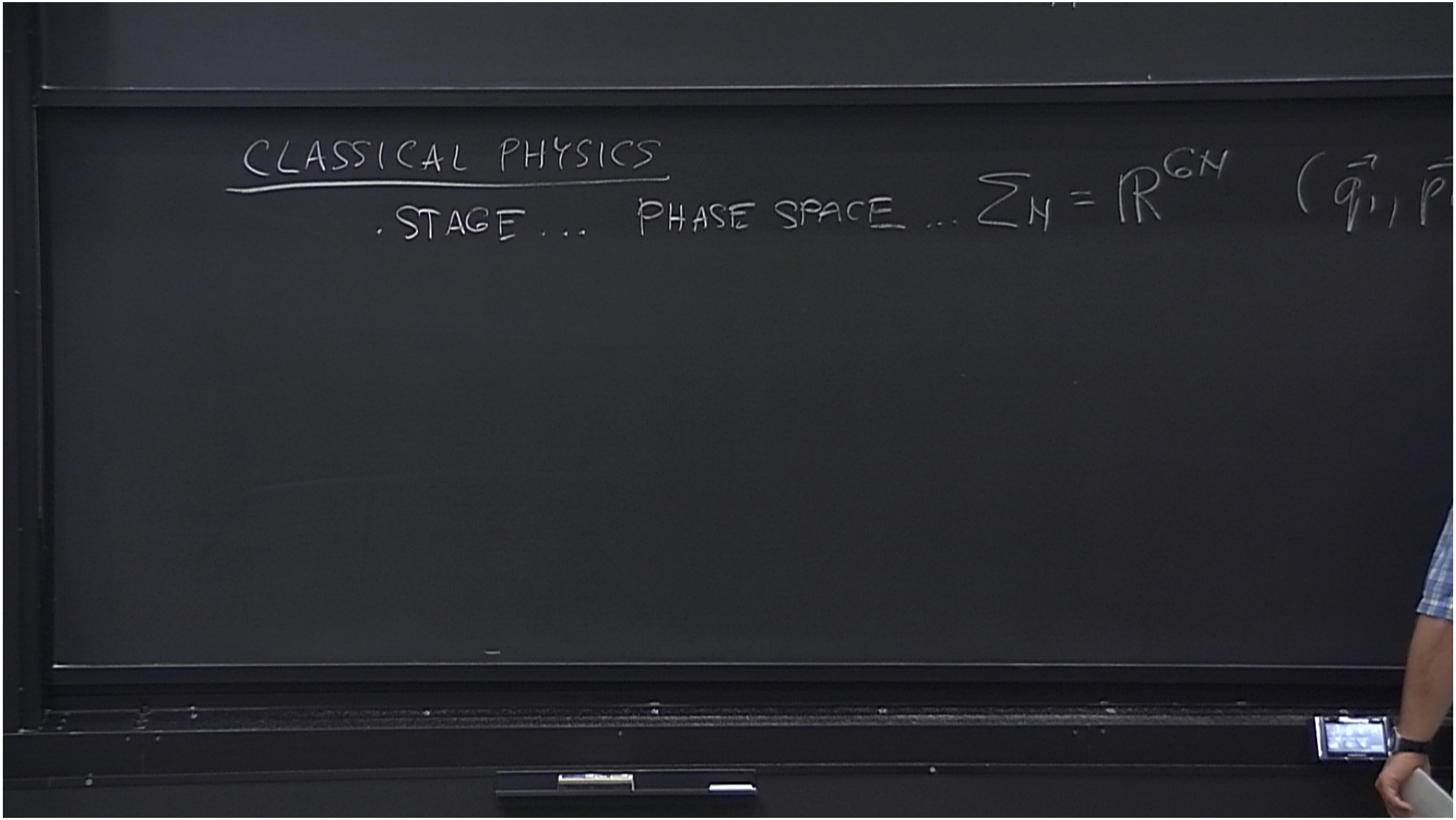

CS
$\mathrm{Tr}\,\rho = 1$
VON NEUMANN EQUATION
$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho]$
TATE $|\psi\rangle \in \mathcal{H}$
RIX $\rho = \sum_x p_x |\psi_x\rangle\langle\psi_x|$
PROBABILITY

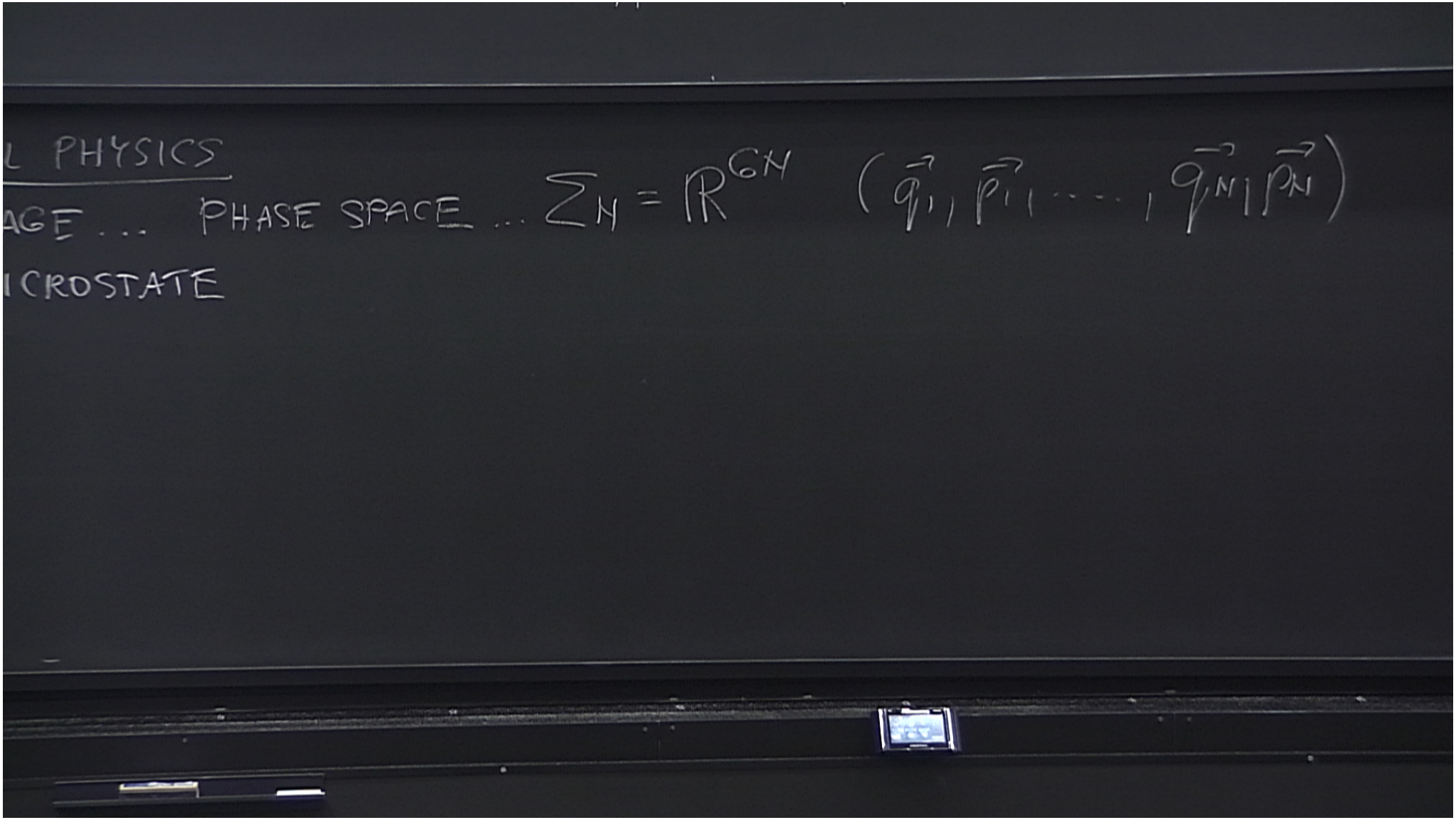

VON NEUMANN
$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho]$
ATE $|\psi\rangle \in \mathcal{H}$
PROBABILITY
RIX $\rho = \sum_x p_x |\psi_x\rangle\langle\psi_x|$
• OBSERVABLES ... OPERATORS

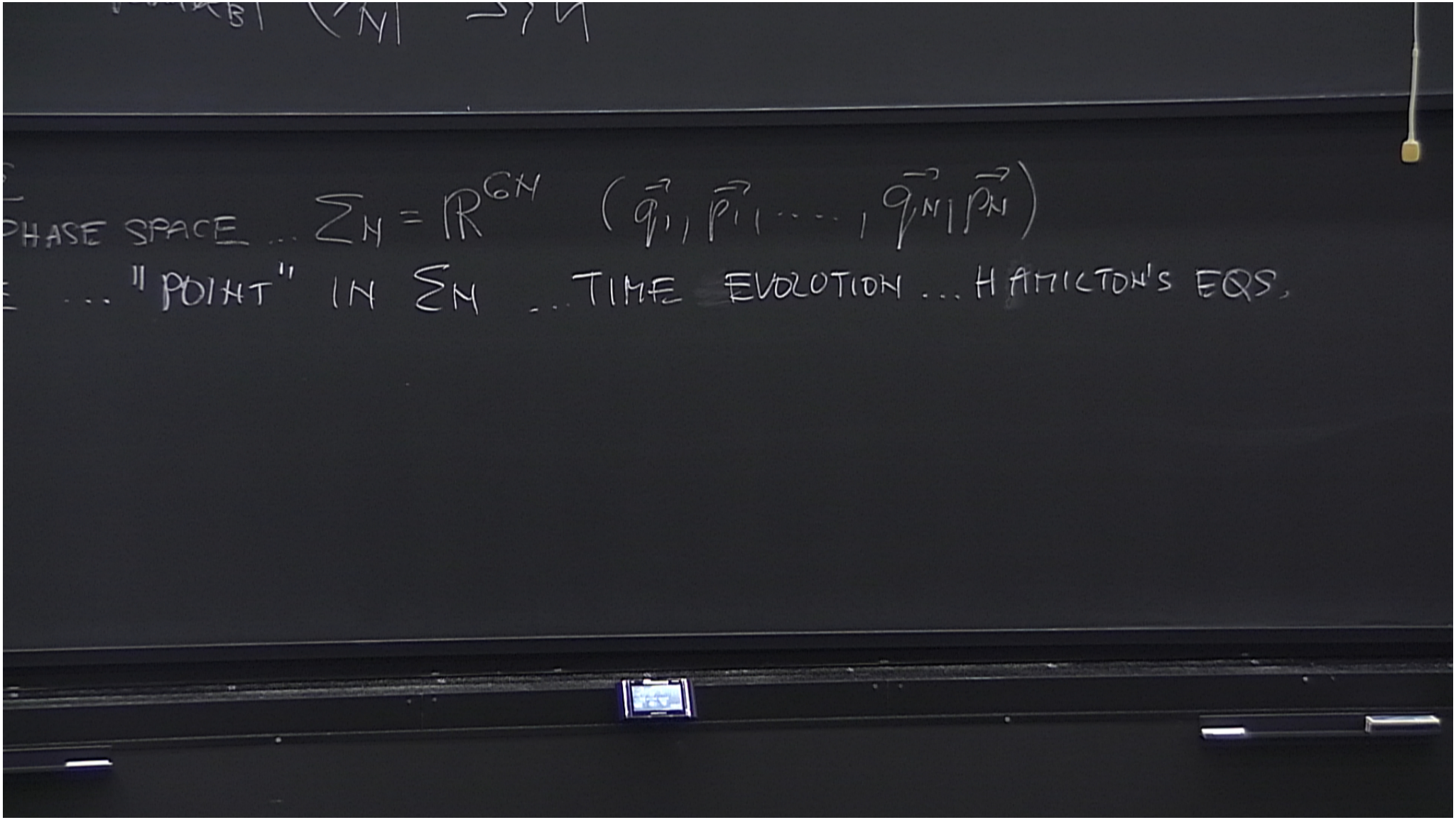

Tr ρ = 1
VON NEUMANN EQUATION
$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho]$
$|\psi\rangle \in \mathcal{H}$
PROBABILITY
$\rho = \sum_x p_x |\psi_x\rangle\langle$
OBSERVABLES ... OPERATORS
⇒ EXPECTATION VALUE
$a = \langle A \rangle = Tr(\rho A)$

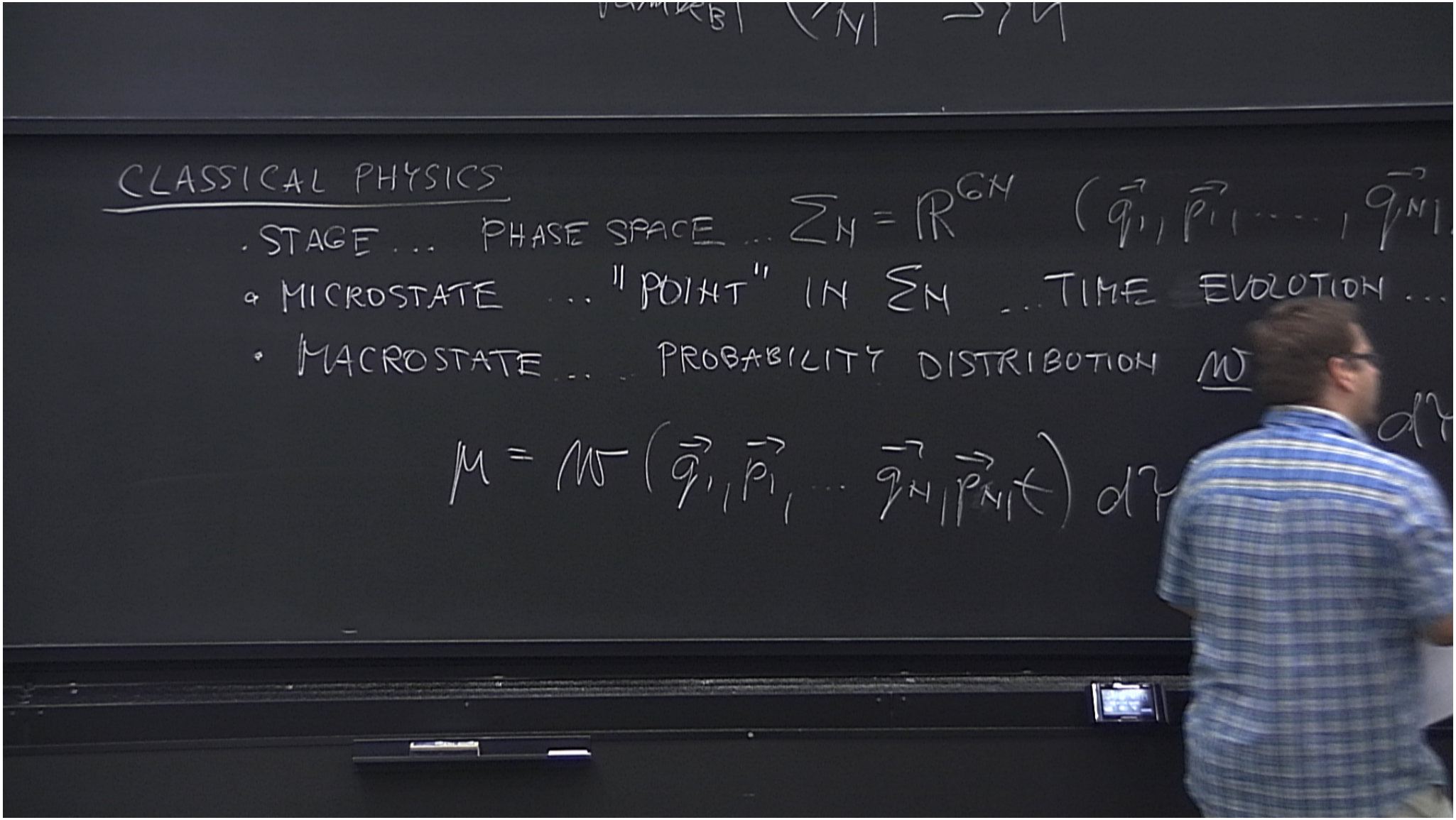

· CLASSICAL PHYSICS APPROXIMATION:
FLUCTUATIONS: $\frac{|\Delta p|^2}{2m} \approx k_B T$
DISTANCE BETWEEN MOLECULES: $\Delta x = \left(\frac{V}{N}\right)^{1/3}$
HEISENBERG: $\Delta x \, \Delta p \gtrsim \hbar$
$\sqrt{2m k_B T}\left(\frac{V}{N}\right)^{1/3} \gg \hbar$


$k_B T \gg \left(\frac{N}{V}\right)^{2/3} \frac{\hbar^2}{2m}$
$\Delta X = \left(\frac{V}{N}\right)^{1/3}$
$\left(\frac{V}{N}\right)^{1/3} \gg \hbar$


CLASSICAL PHYSICS
. STAGE ... PHASE SPACE ... $\Sigma_N = \mathbb{R}^{6N}$ $(\vec{q}_i, \vec{p}$


L PHYSICS
AGE ... PHASE SPACE ... $\Sigma_N = \mathbb{R}^{6N}$ $(\vec{q}_1, \vec{p}_1, \ldots, \vec{q}_N, \vec{p}_N)$
ICROSTATE


PHASE SPACE ... $\Sigma_N = \mathbb{R}^{6N}$ $(\vec{q}_1, \vec{p}_1, \ldots, \vec{q}_N, \vec{p}_N)$
... "POINT" IN Σ_N ... TIME EVOLOTION ... HAMILTON'S EQS.


CLASSICAL PHYSICS
. STAGE ... PHASE SPACE ... $\Sigma_N = \mathbb{R}^{6N}$ $(\vec{q}_1, \vec{p}_1, \ldots, \vec{q}_N$
. MICROSTATE ... "POINT" IN Σ_N ... TIME EVOLOTION ...
. MACROSTATE ... PROBABILITY DISTRIBUTION ρ
$\mu = \rho(\vec{q}_1, \vec{p}_1, \ldots \vec{q}_N, \vec{p}_N, t)\, d\Gamma$

$\Sigma_N = \mathbb{R}^{6N} \quad (\vec{q}_1, \vec{p}_1, \ldots, \vec{q}_N, \vec{p}_N)$

IN Σ_N ... TIME EVOLOTION ... HAMILTON'S EQS.

ILITY DISTRIBOTION $\underline{W}$

$\ldots \vec{q}_N, \vec{p}_N, t)\, d\Gamma_N,$

$$d\Gamma_N = \frac{1}{N!\,(2\pi\hbar)^{3N}}\, d^3p_1 d^3q_1 \ldots d^3p_N d^3q_N$$

$\Sigma_N = \mathbb{R}^{6N} \quad (\vec{q}_1, \vec{p}_1, \ldots, \vec{q}_N, \vec{p}_N)$

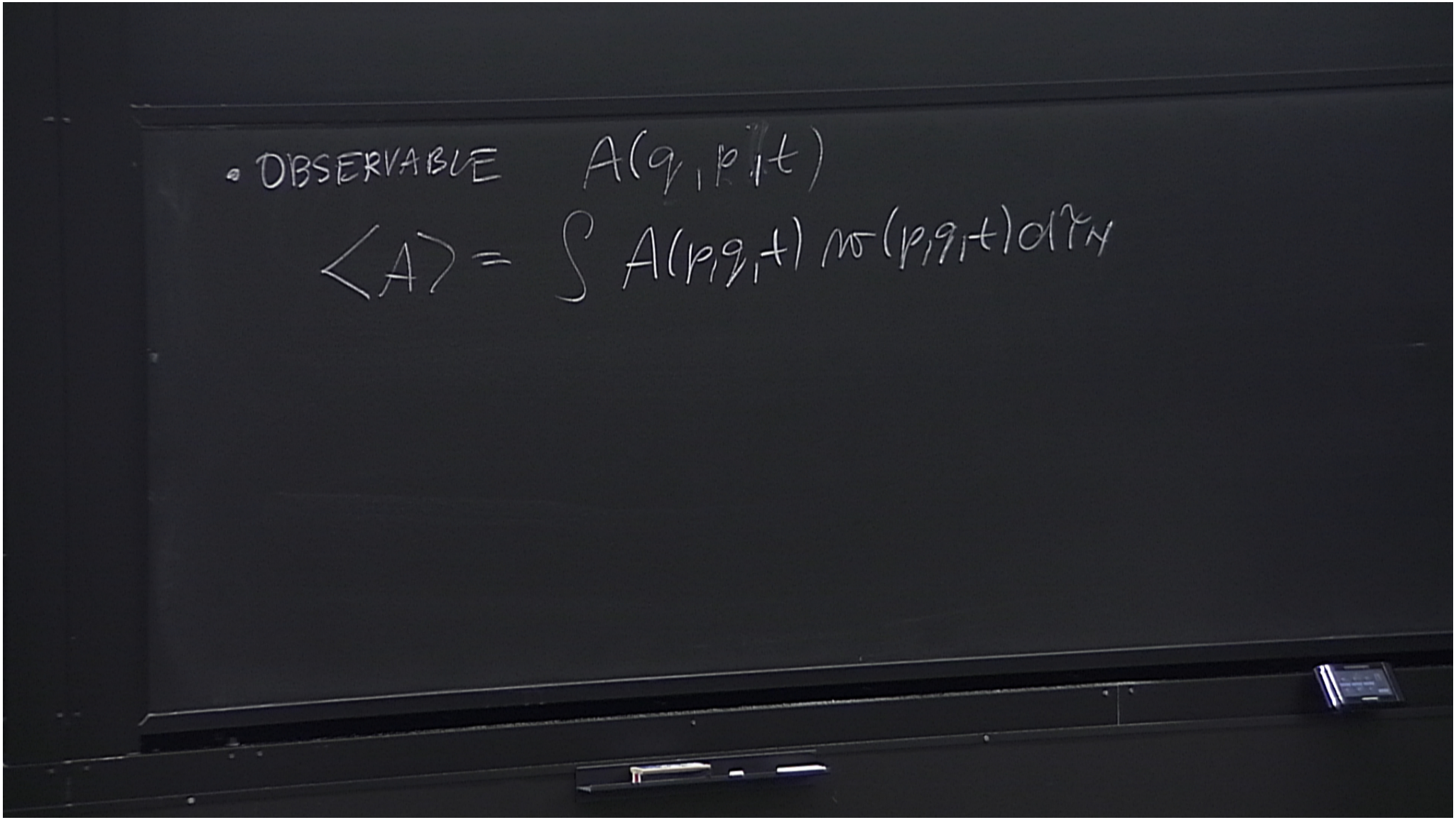
IN Σ_N ... TIME EVOLOTION ... HAMILTON'S EQS.

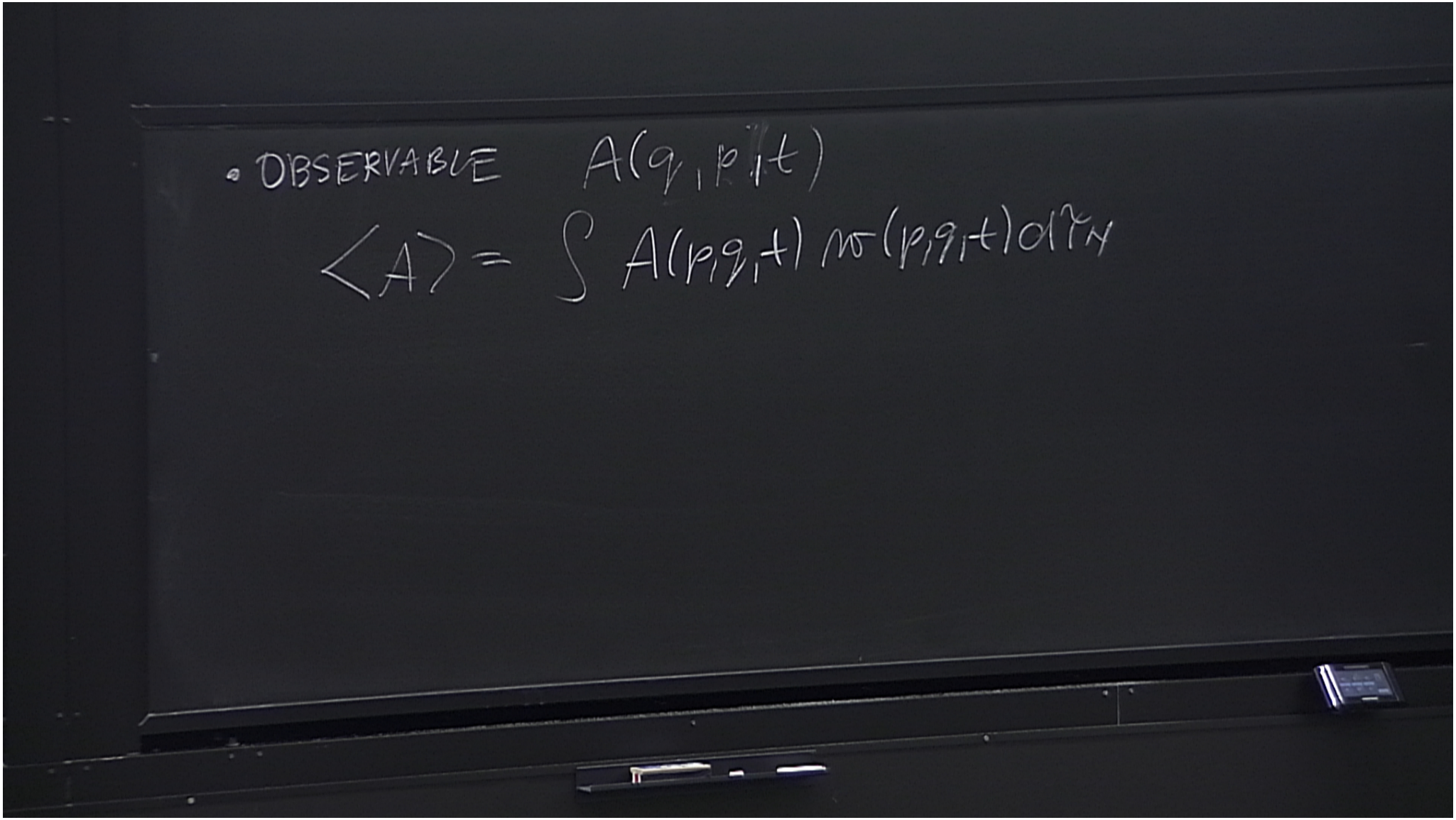
ILITY DISTRIBOTION ω

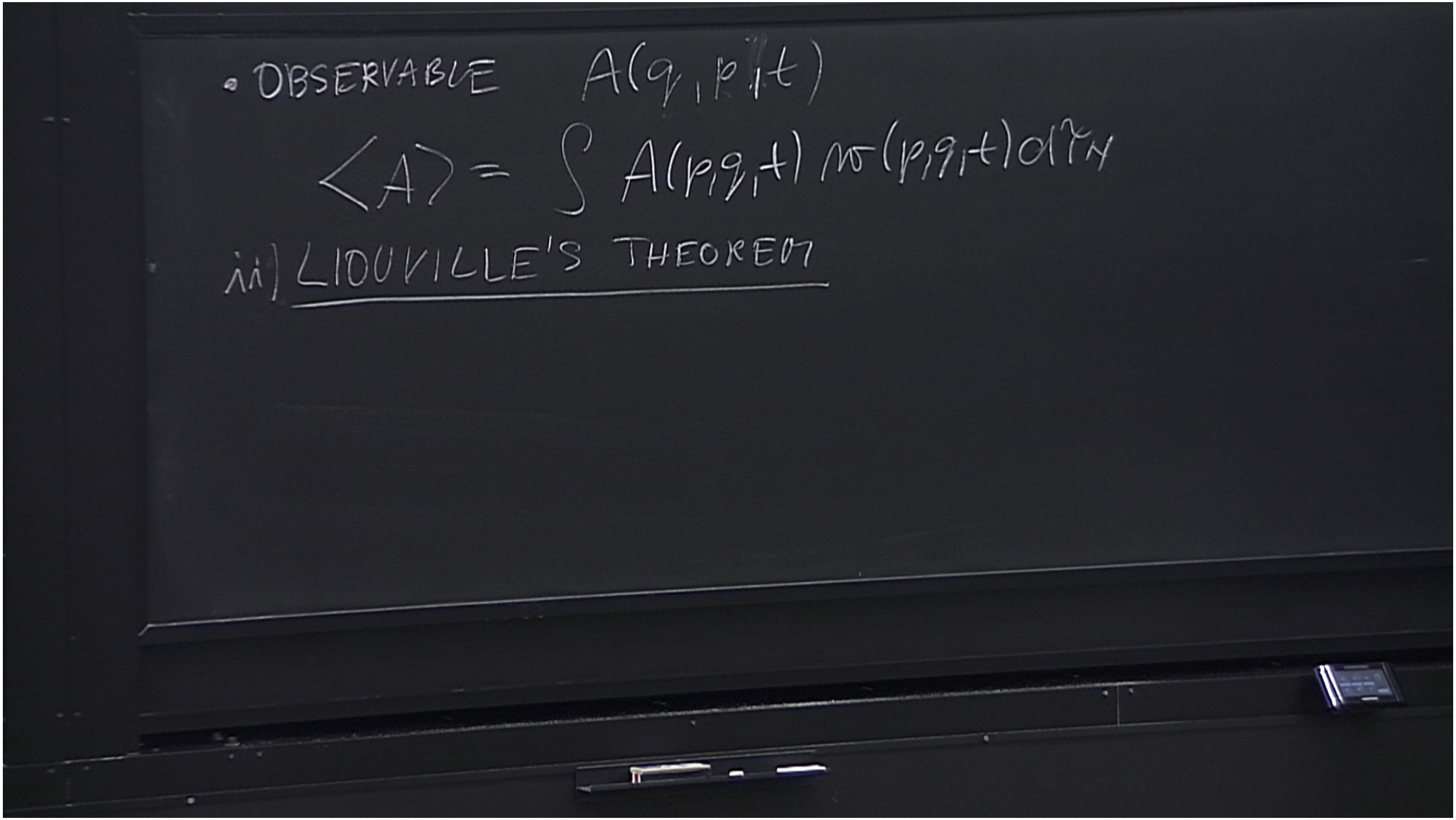
$\ldots \vec{q}_N, \vec{p}_N, t) \, d\Gamma_N$,

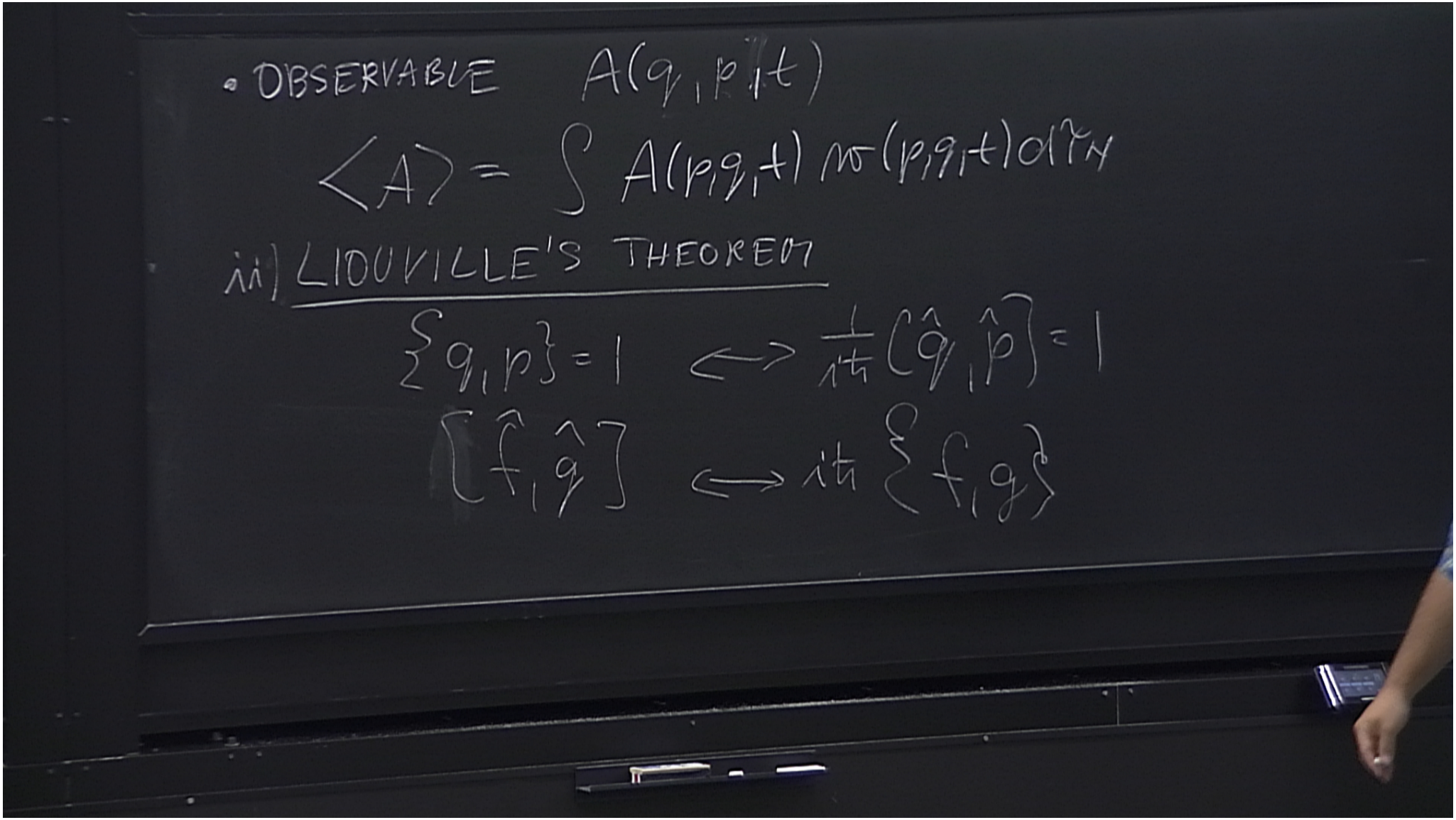
$$d\Gamma_N = \frac{1}{N! \, (2\pi\hbar)^{3N}} \, d^3p_1 d^3q_1 \ldots d^3p_N d^3q_N$$

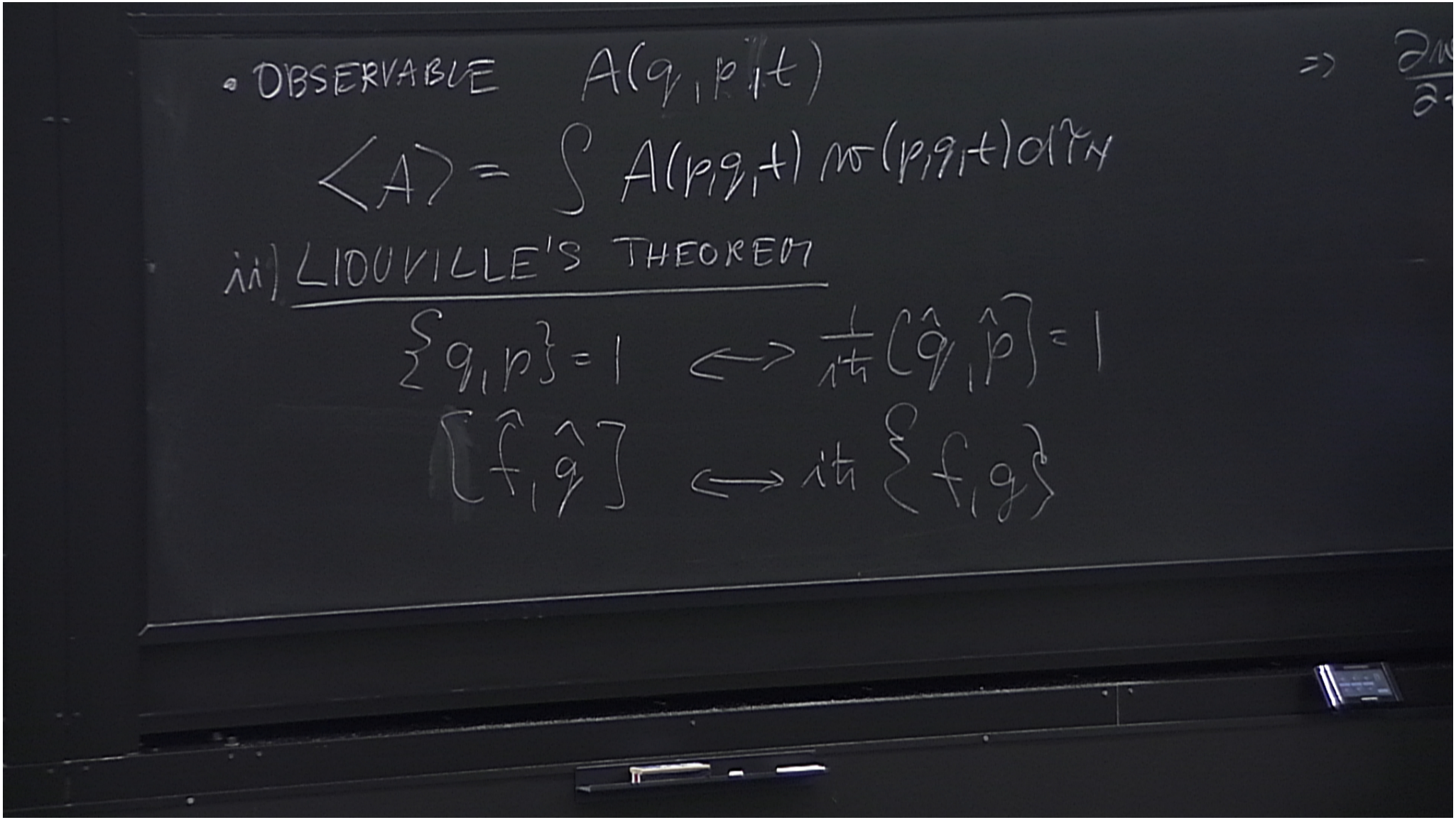
$$\int \omega \, d\Gamma_N = 1$$


• OBSERVABLE A(q, p, t)
⟨A⟩ = ∫ A(p, q, t) ρ(p, q, t) dΓ_N


• OBSERVABLE A(q, p, t)
⟨A⟩ = ∫ A(p, q, t) ρ(p, q, t) d^{3N}


• OBSERVABLE $A(q, p, t)$
$\langle A \rangle = \int A(p,q,t)\, \rho(p,q,t)\, d\Gamma_N$
ii) LIOUVILLE'S THEOREM

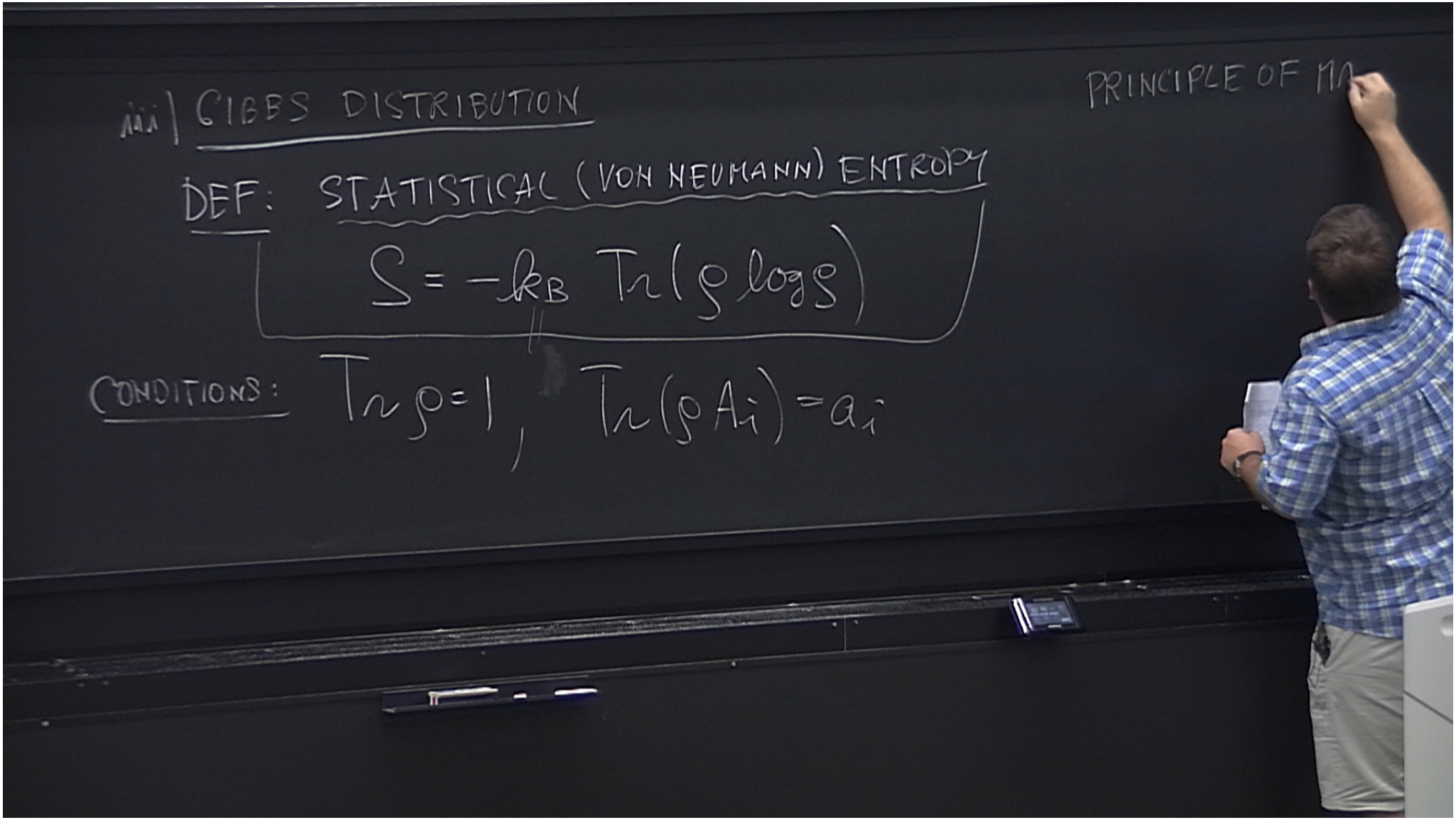

• OBSERVABLE A(q, p, t)
⟨A⟩ = ∫ A(p, q, t) ρ(p, q, t) d^{3N}
ii) LIOUVILLE'S THEOREM
{q, p} = 1 ⟺ (1/iħ)[q̂, p̂] = 1
[f̂, ĝ] ⟺ iħ {f, g}

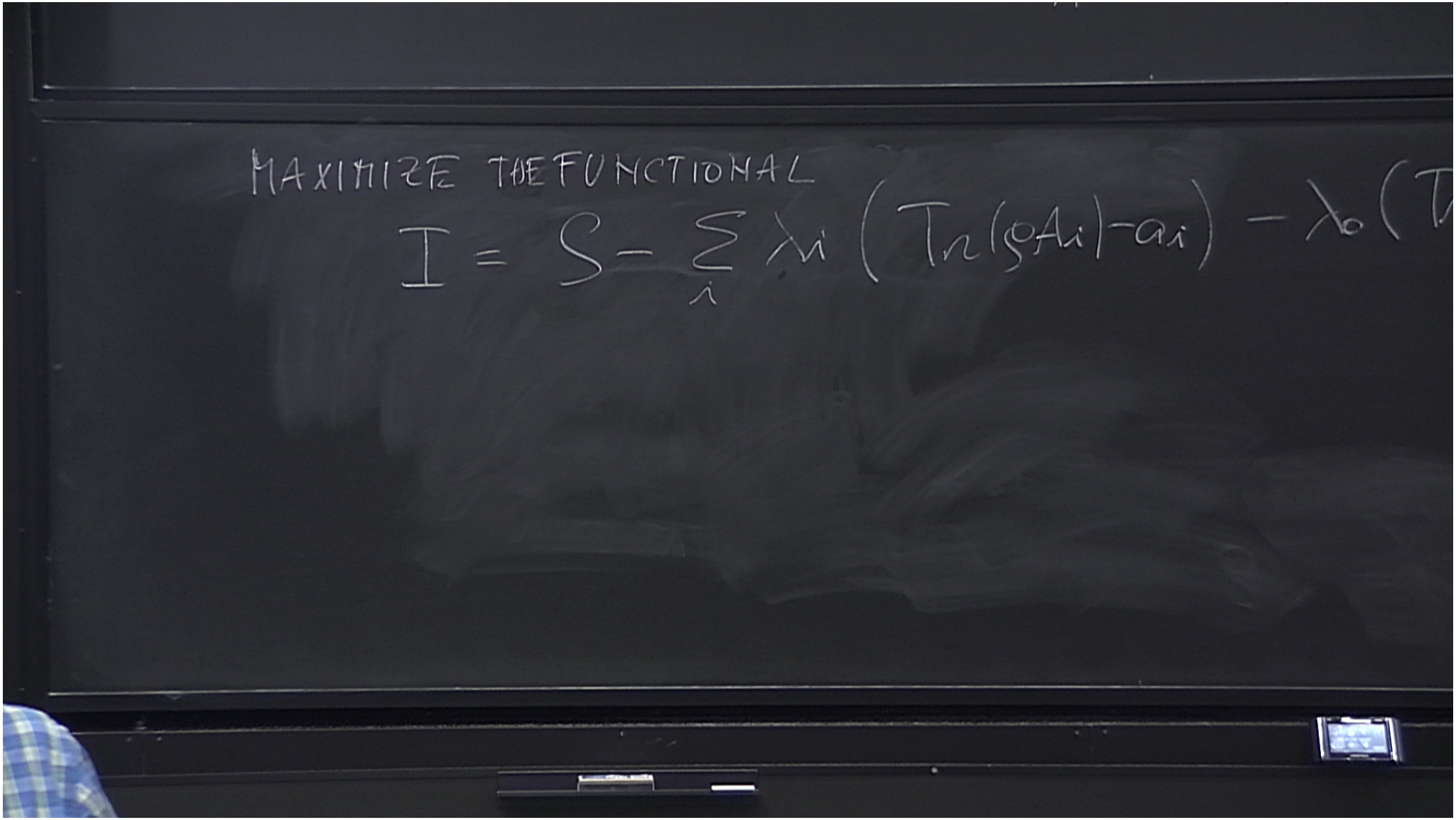

• OBSERVABLE A(q, p, t)
⟨A⟩ = ∫ A(p, q, t) ρ(p, q, t) d^{3N}
ii) LIOUVILLE'S THEOREM
{q, p} = 1 ⟺ (1/iħ)[q̂, p̂] = 1
[f̂, ĝ] ⟺ iħ {f, g}

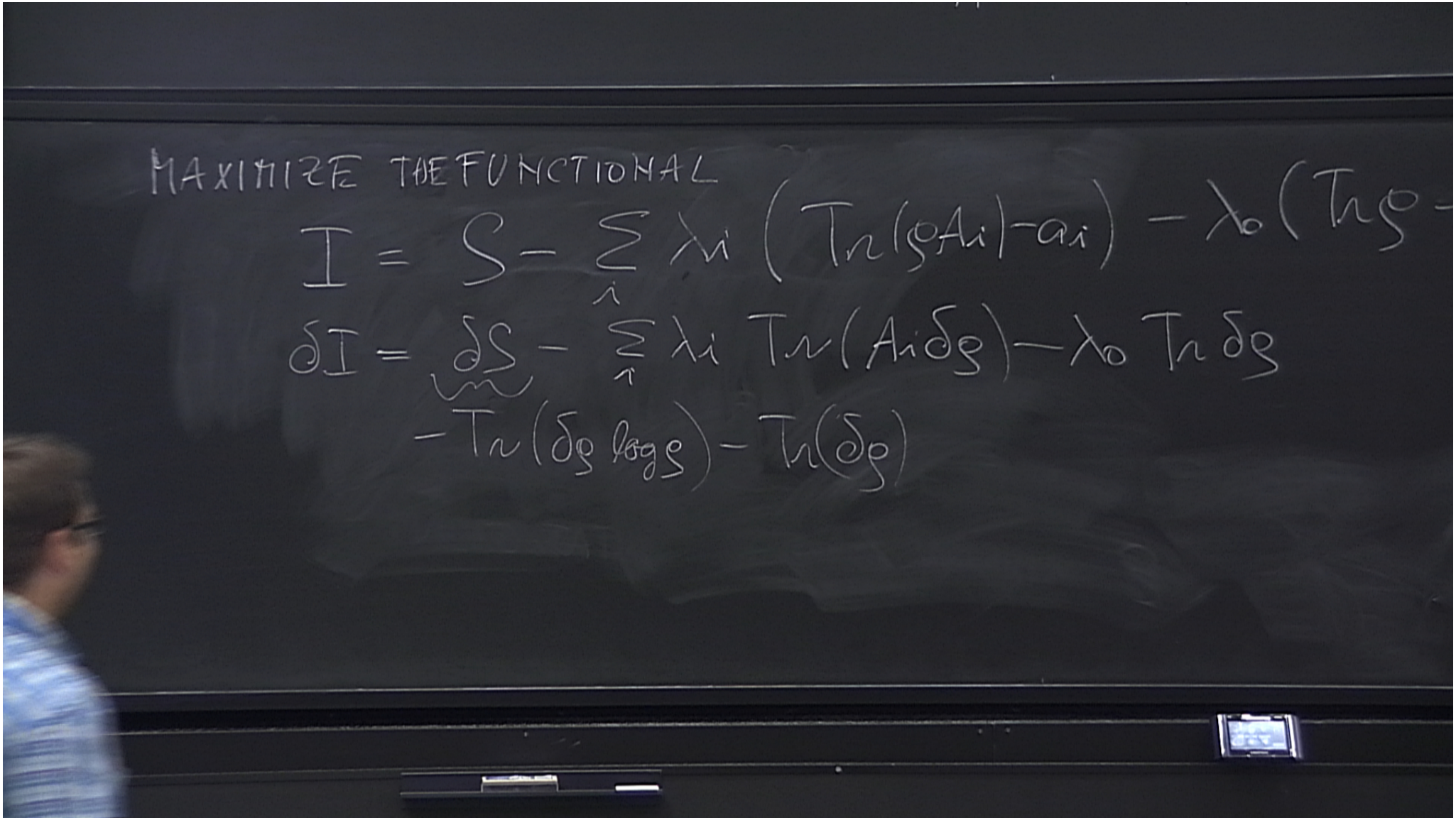
iii) GIBBS DISTRIBUTION

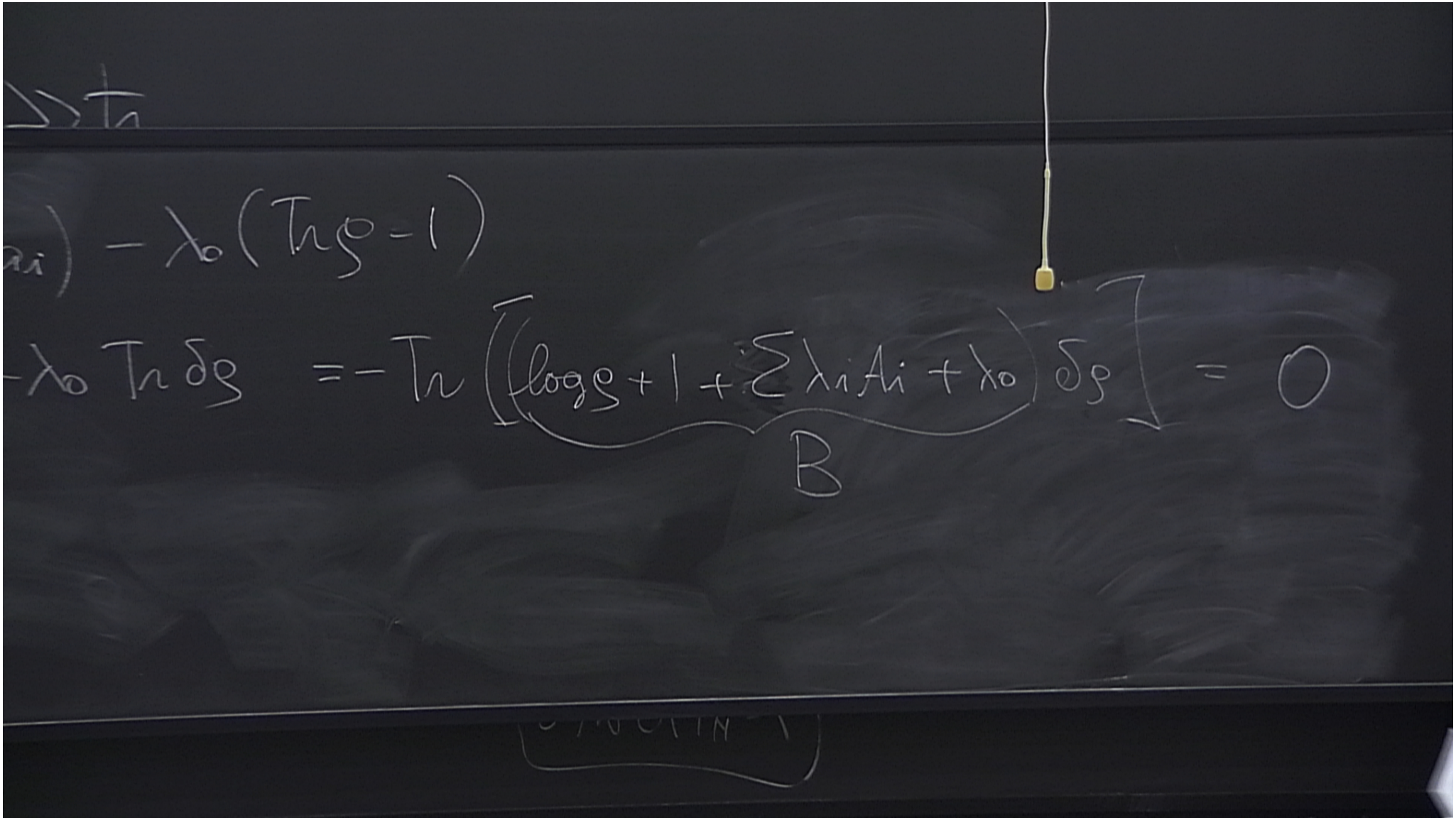
DEF: STATISTICAL (VON NEUMANN) ENTROPY

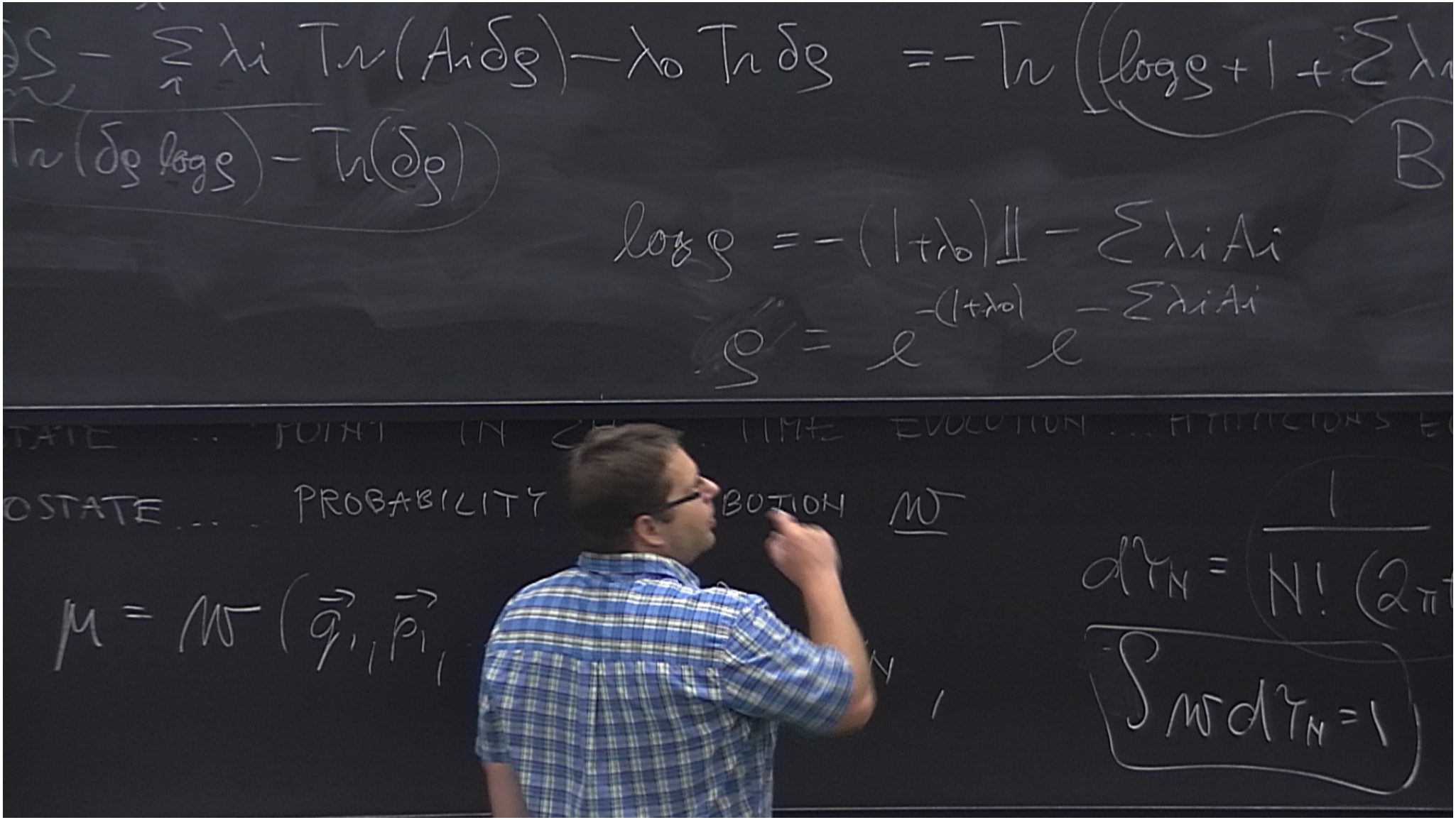
$$S = -k_B \, \mathrm{Tr}(\rho \log \rho)$$

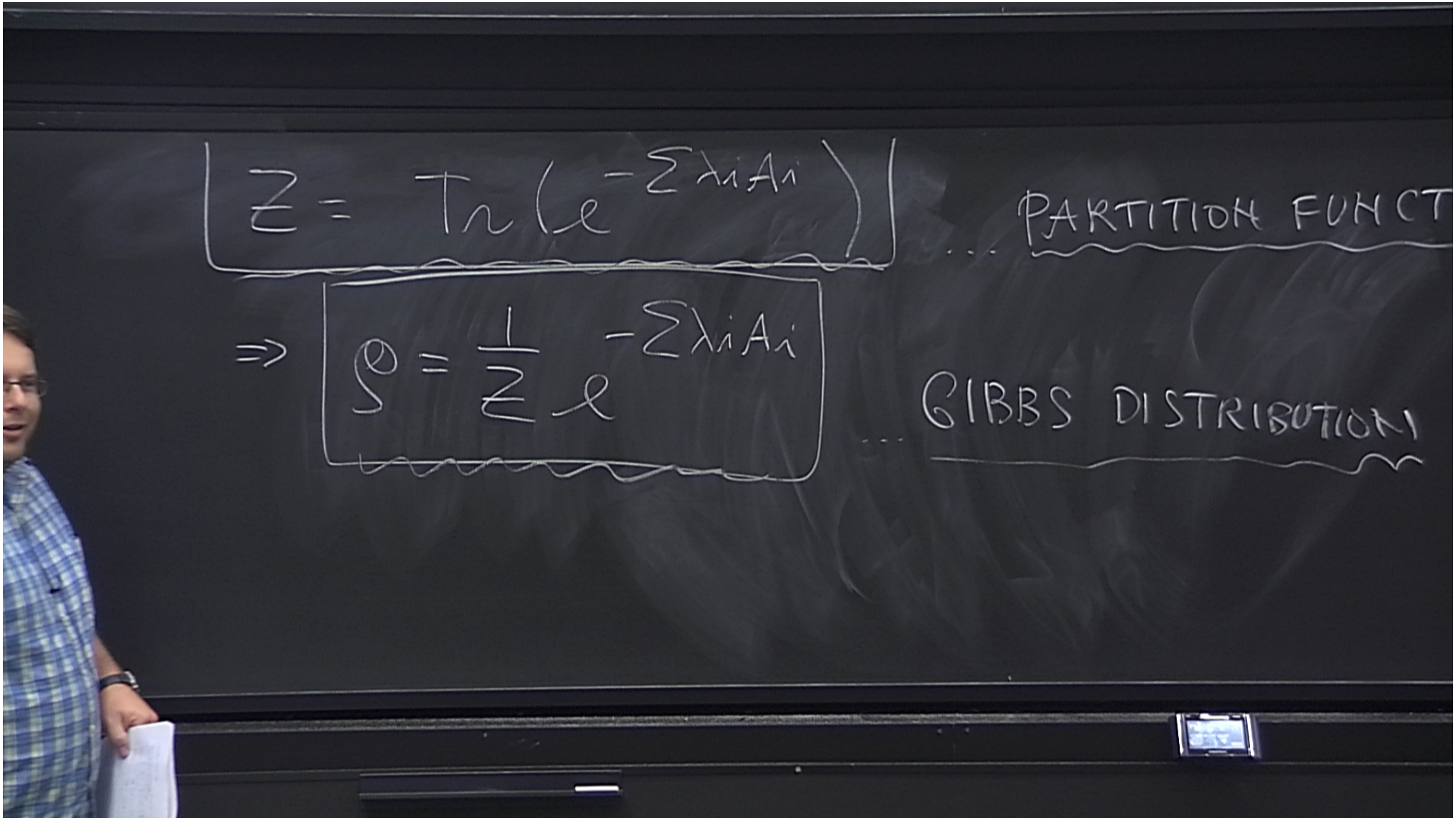

iii) GIBBS DISTRIBUTION
PRINCIPLE OF MA
DEF: STATISTICAL (VON NEUMANN) ENTROPY
$S = -k_B \mathrm{Tr}(\rho \log \rho)$
CONDITIONS: $\mathrm{Tr}\,\rho = 1$, $\mathrm{Tr}(\rho A_i) = a_i$

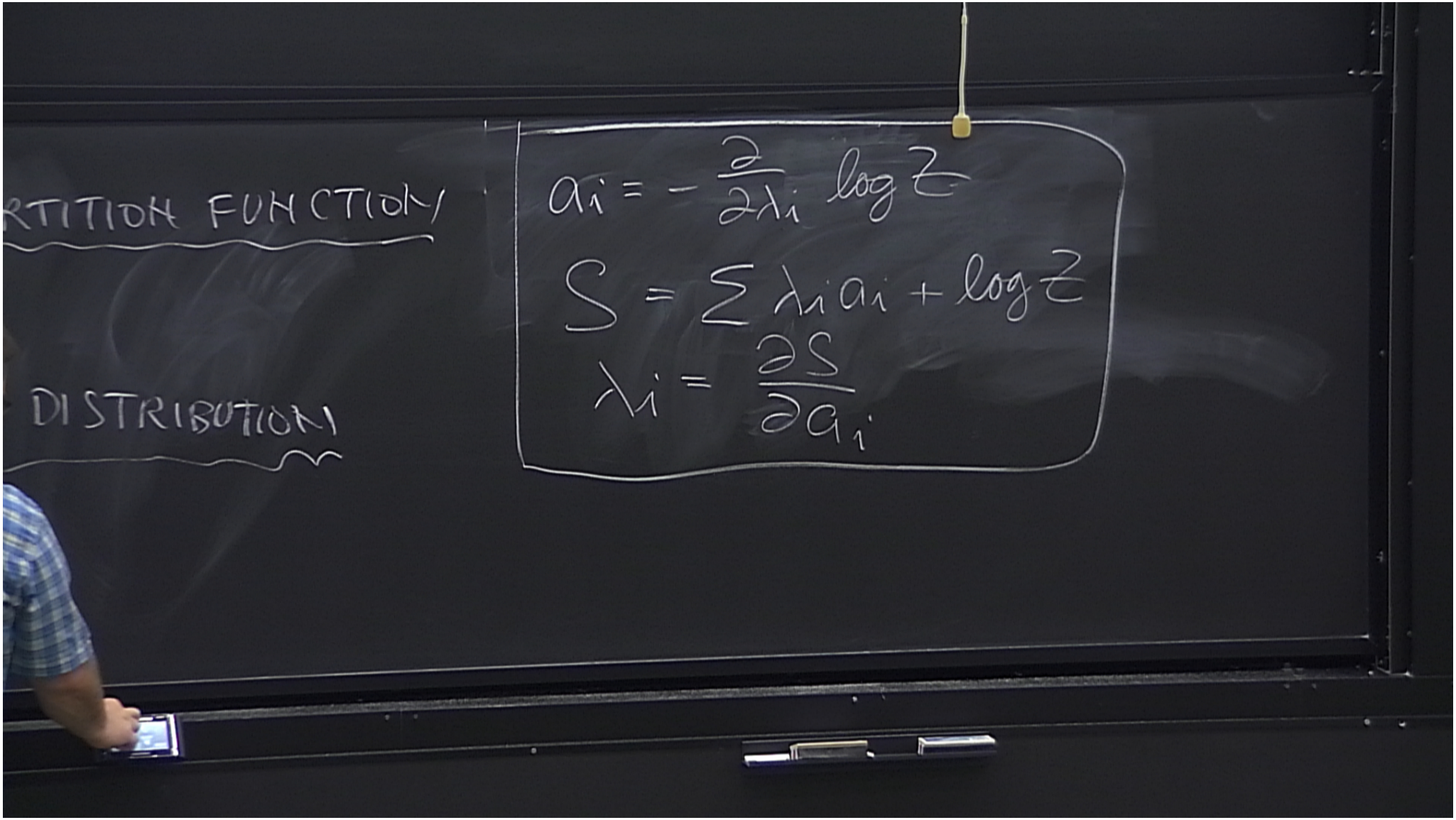

MAXIMIZE THE FUNCTIONAL
$I = S - \sum_i \lambda_i \left(Tr(\rho A_i) - a_i \right) - \lambda_0 ($

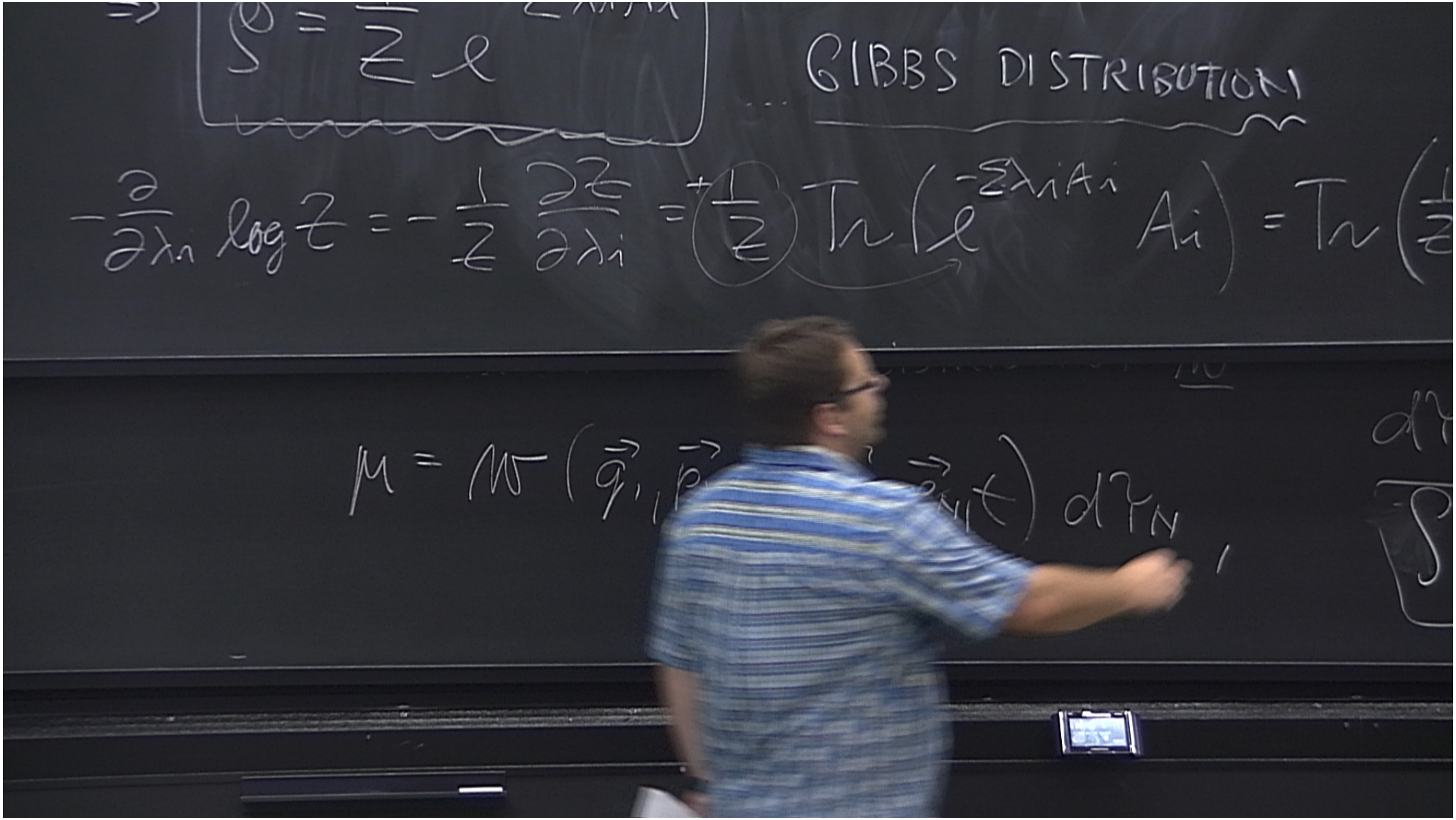

MAXIMIZE THE FUNCTIONAL
$I = S - \sum_i \lambda_i \left(Tr(\rho A_i) - a_i \right) - \lambda_0 (Tr\rho -$
$\delta I = \delta S - \sum_i \lambda_i Tr(A_i \delta\rho) - \lambda_0 Tr\,\delta\rho$
$- Tr(\delta\rho \log\rho) - Tr(\delta\rho)$

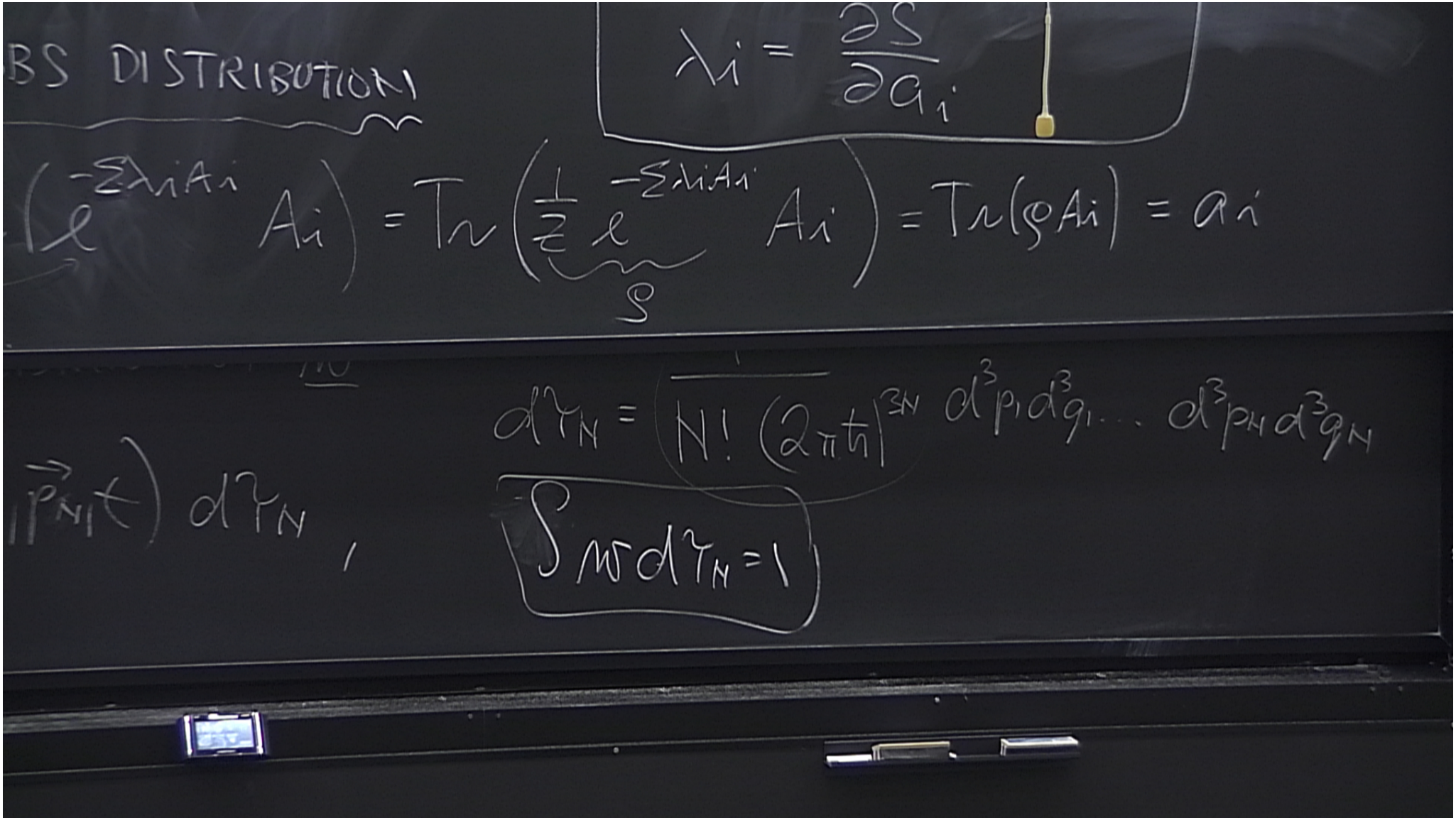

$\rho_i) - \lambda_0 (\mathrm{Tr}\rho - 1)$
$-\lambda_0 \mathrm{Tr}\delta\rho = -\mathrm{Tr}\left[\underbrace{(\log\rho + 1 + \sum \lambda_i A_i + \lambda_0)}_{B}\delta\rho\right] = 0$

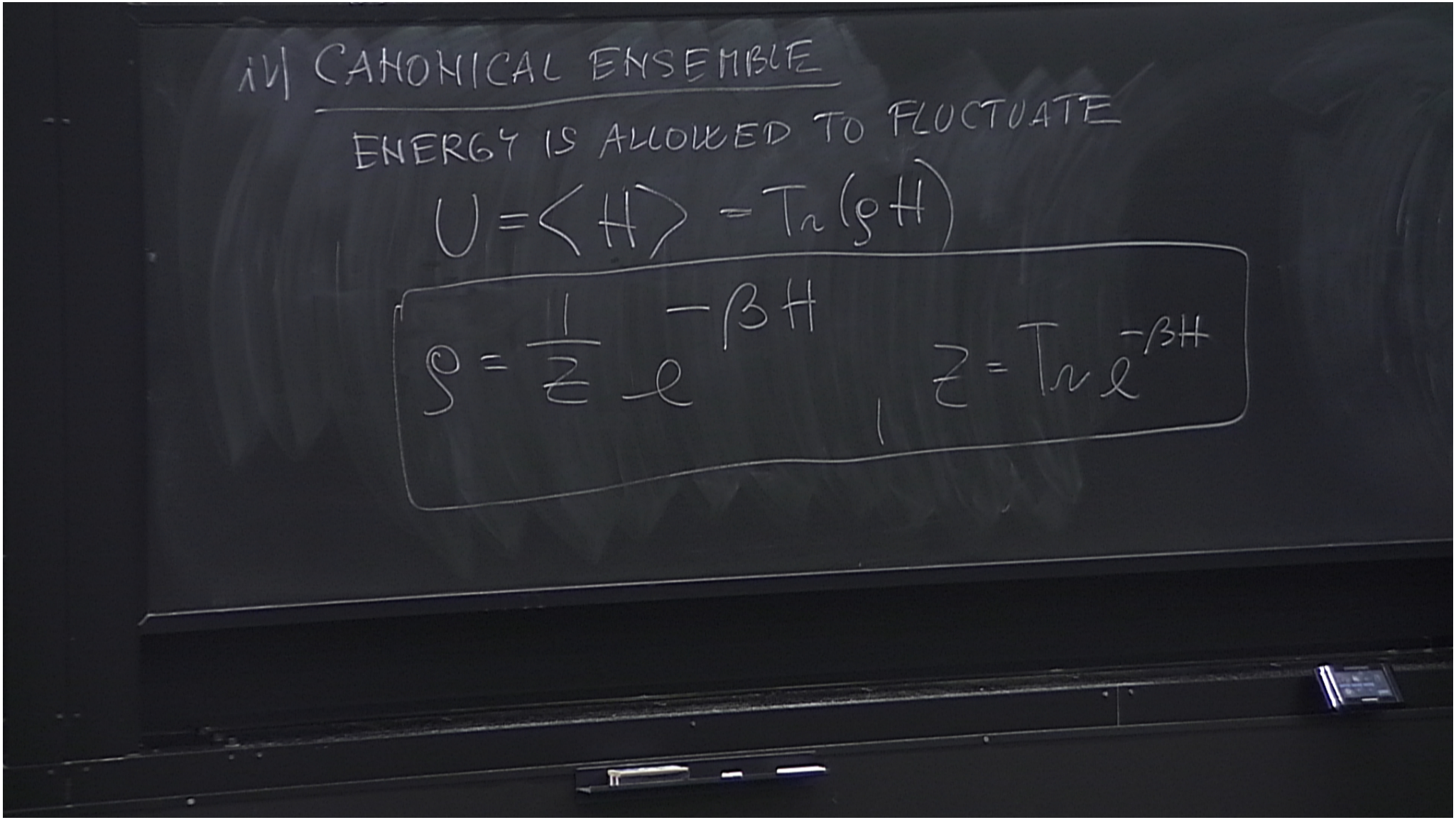

$\delta S - \sum \lambda_i \mathrm{Tr}(A_i \delta\rho) - \lambda_0 \mathrm{Tr}\,\delta\rho = -\mathrm{Tr}(\log\rho + 1 + \sum \lambda_i$
$\mathrm{Tr}(\delta\rho \log\rho) - \mathrm{Tr}(\delta\rho)$
B
$\log\rho = -(1+\lambda_0)\mathbb{1} - \sum \lambda_i A_i$
$\rho = e^{-(1+\lambda_0)} e^{-\sum \lambda_i A_i}$
PROBABILITY
$\mu = \mathcal{W}(\vec{q}_1, \vec{p}_1,$
$d\Gamma_N = \frac{1}{N!(2\pi$
$\int \mathcal{W} d\Gamma_N = 1$

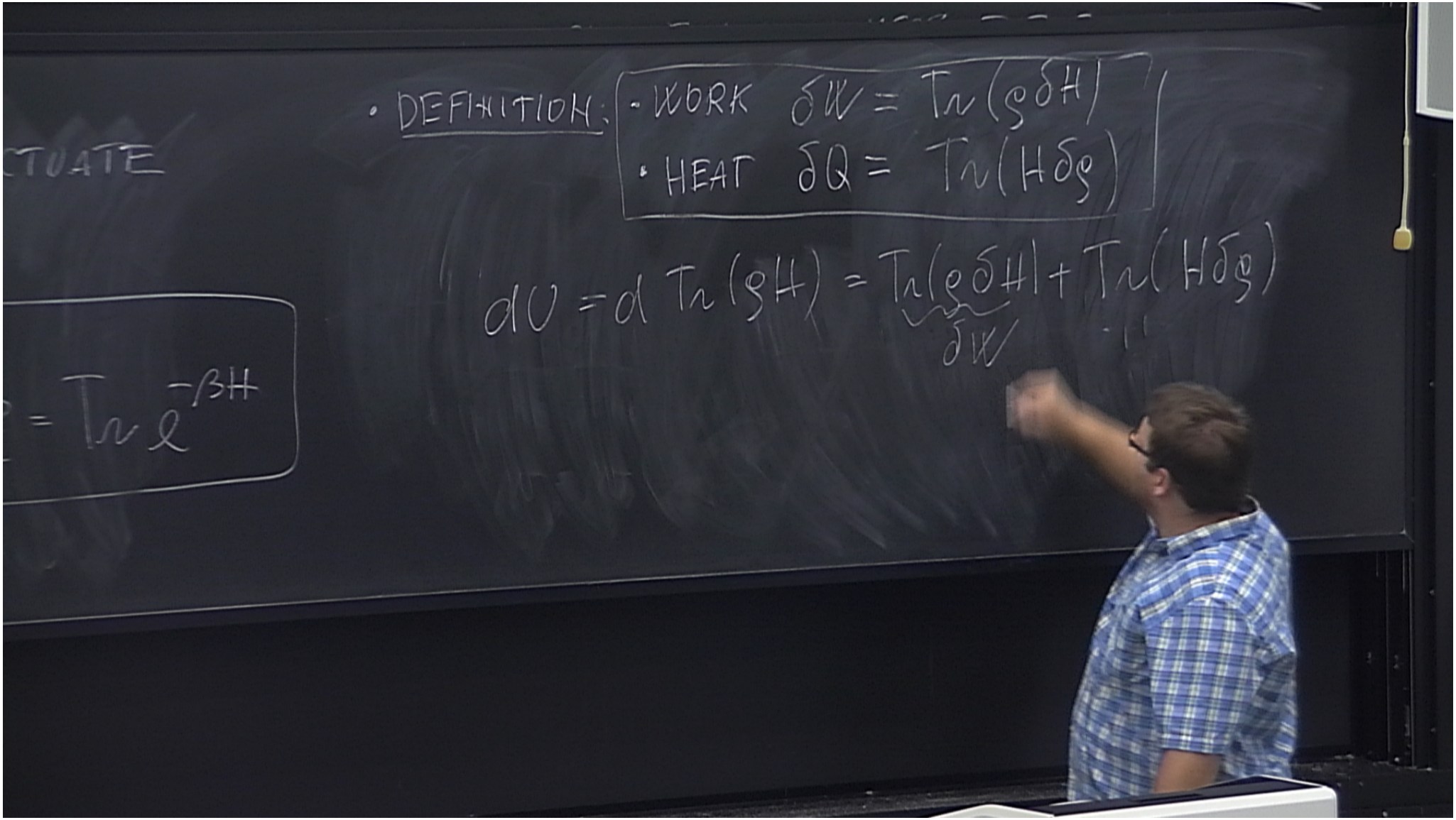

$Z = Tr(e^{-\Sigma \lambda_i A_i})$
... PARTITION FUNCT
$\Rightarrow \rho = \frac{1}{Z} e^{-\Sigma \lambda_i A_i}$
... GIBBS DISTRIBUTION

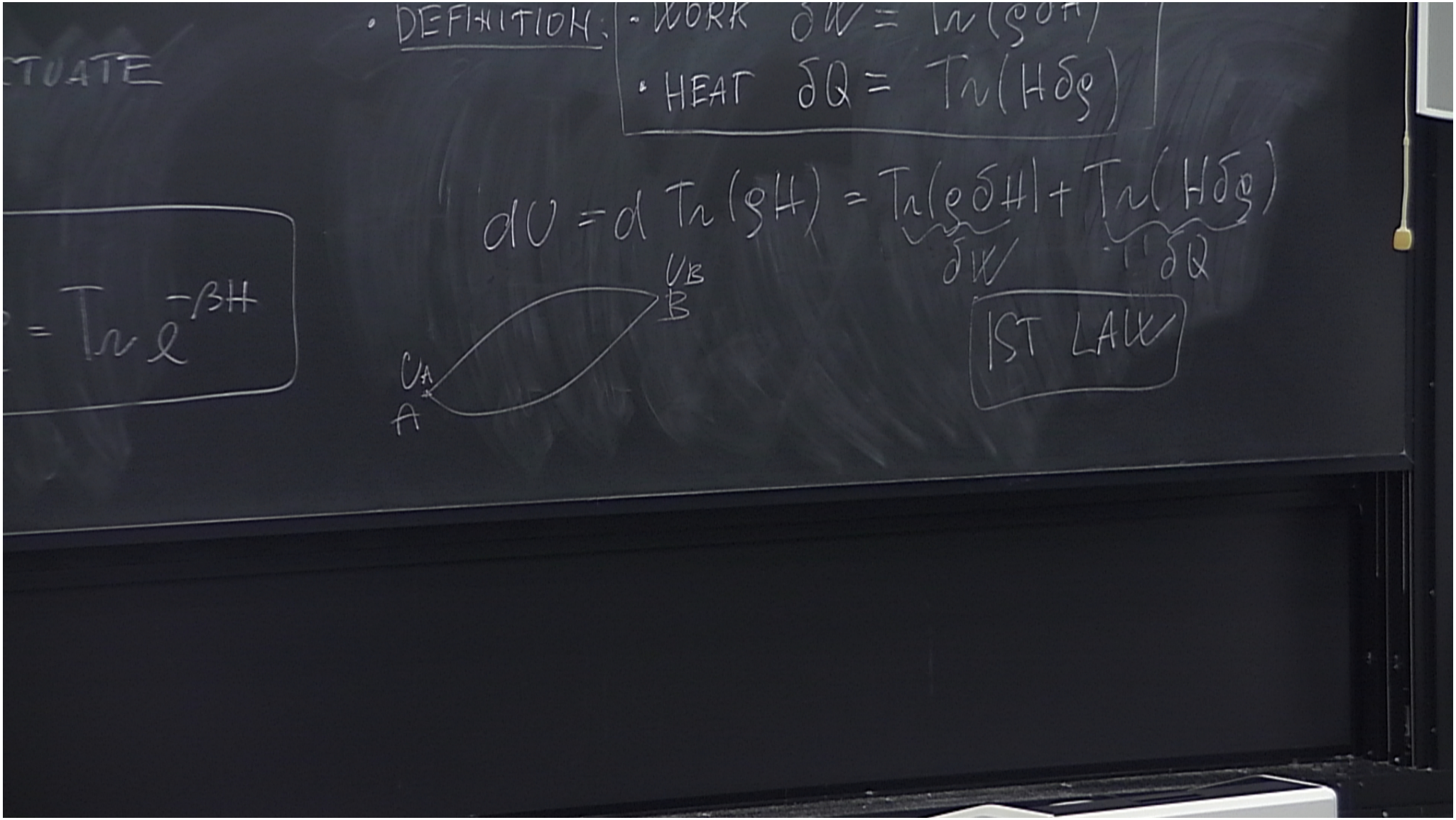

RTITION FUNCTION
DISTRIBUTION
$a_i = -\frac{\partial}{\partial \lambda_i} \log Z$
$S = \Sigma \lambda_i a_i + \log Z$
$\lambda_i = \frac{\partial S}{\partial a_i}$


GIBBS DISTRIBUTION


BS DISTRIBUTION
$\lambda_i = \frac{\partial S}{\partial a_i}$
$\left(e^{-\Sigma\lambda_i A_i} A_i\right) = \mathrm{Tr}\left(\frac{1}{Z} e^{-\Sigma\lambda_i A_i} A_i\right) = \mathrm{Tr}(\rho A_i) = a_i$
ρ
$d\tau_N = \frac{1}{N!\,(2\pi\hbar)^{3N}} d^3p_1 d^3q_1 \ldots d^3p_N d^3q_N$
$\vec{p}_N, t)\, d\tau_N$,
$\int w\, d\tau_N = 1$


iv) CANONICAL ENSEMBLE
ENERGY IS ALLOWED TO FLUCTUATE
$U = \langle H \rangle = Tr(\rho H)$
$\rho = \frac{1}{Z} e^{-\beta H}$, $Z = Tr\, e^{-\beta H}$


• DEFINITION:
• WORK $\delta W = \mathrm{Tr}(\rho\,\delta H)$
• HEAT $\delta Q = \mathrm{Tr}(H\,\delta\rho)$
$dU = d\,\mathrm{Tr}(\rho H) = \mathrm{Tr}(\rho\,\delta H) + \mathrm{Tr}(H\,\delta\rho)$
δW
$= \mathrm{Tr}\, e^{-\beta H}$


· DEFINITION:
· WORK
· HEAT $\delta Q = \mathrm{Tr}(H\delta\varrho)$
$dU = d\,\mathrm{Tr}(\varrho H) = \mathrm{Tr}(\varrho\,\delta H) + \mathrm{Tr}(H\delta\varrho)$
δW
δQ
IST LAW
$= \mathrm{Tr}\,e^{-\beta H}$
U_B
B
U_A
A

PRINCIPLE OF MAXIMAL MESS: THE DENSITY MATRIX

ϱ REPRESENTING THE EQUILIBRIUM STATE

(MANN) ENTROPY

IC SUCH THAT IT MAXIMIZES

CTUATE

• DEFINITION:

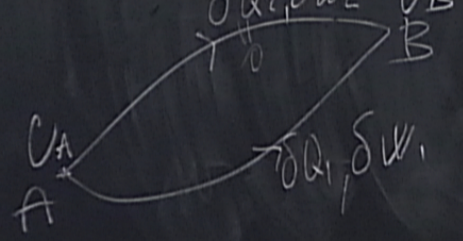
- WORK $\delta W = \mathrm{Tr}(\varrho\, \delta H) = \sum_m \delta \ell_m\, p_m$
- HEAT $\delta Q = \mathrm{Tr}(H \delta\varrho) = \sum_m \delta p_m\, \ell_m$

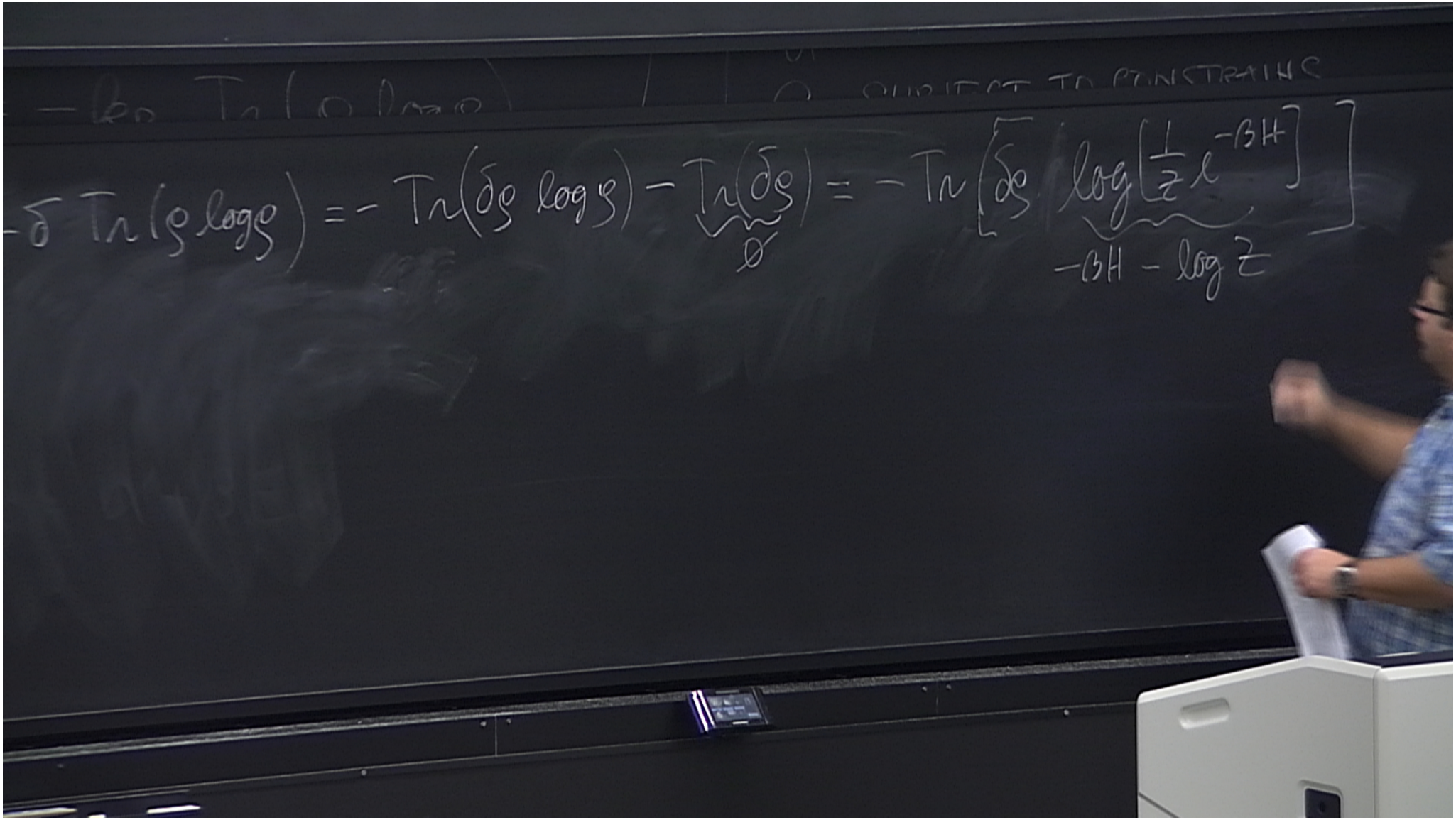
$$dU = d\,\mathrm{Tr}(\varrho H) = \mathrm{Tr}(\varrho\, \delta H) + \mathrm{Tr}(H \delta\varrho)$$

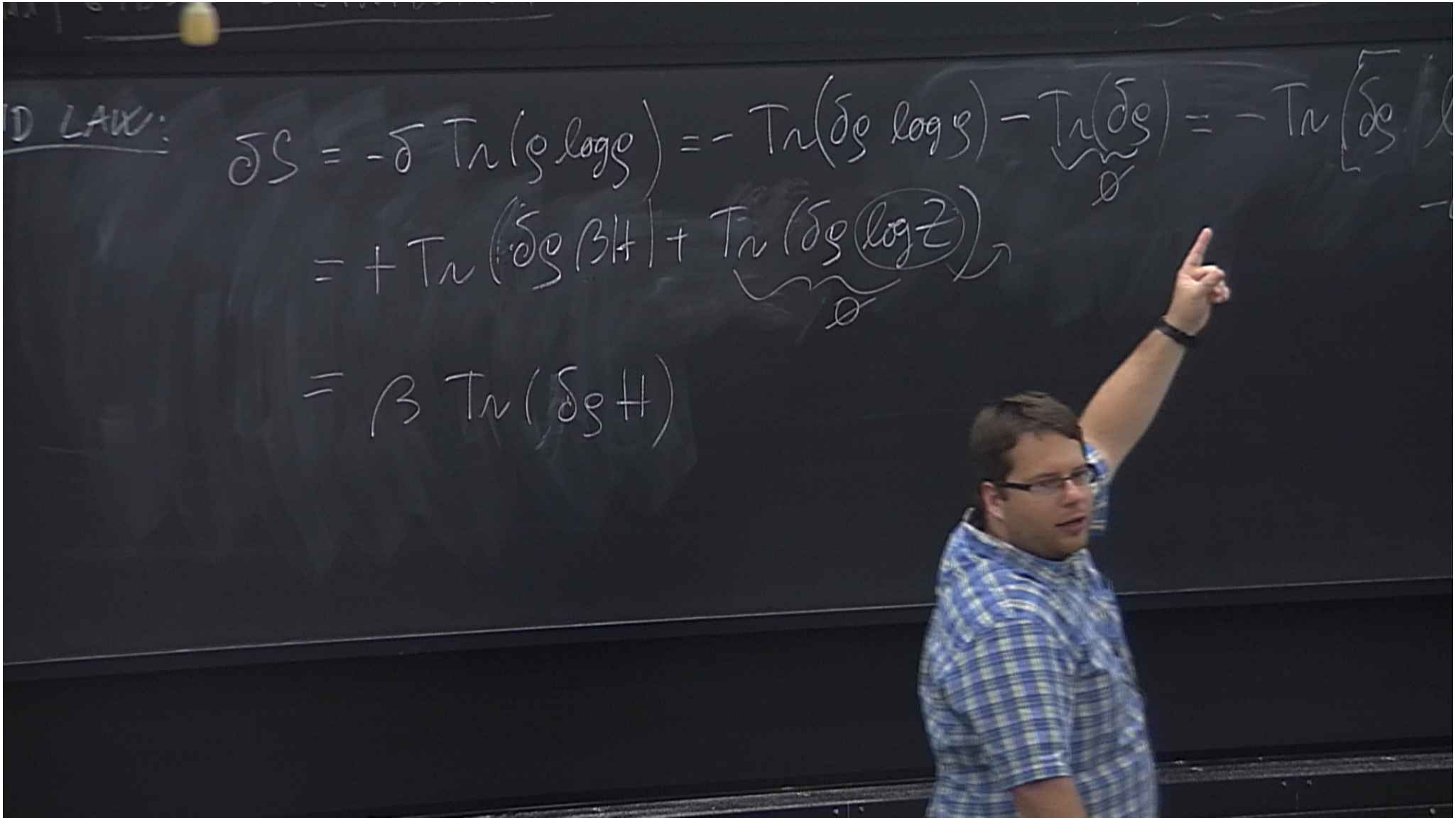
δW δQ

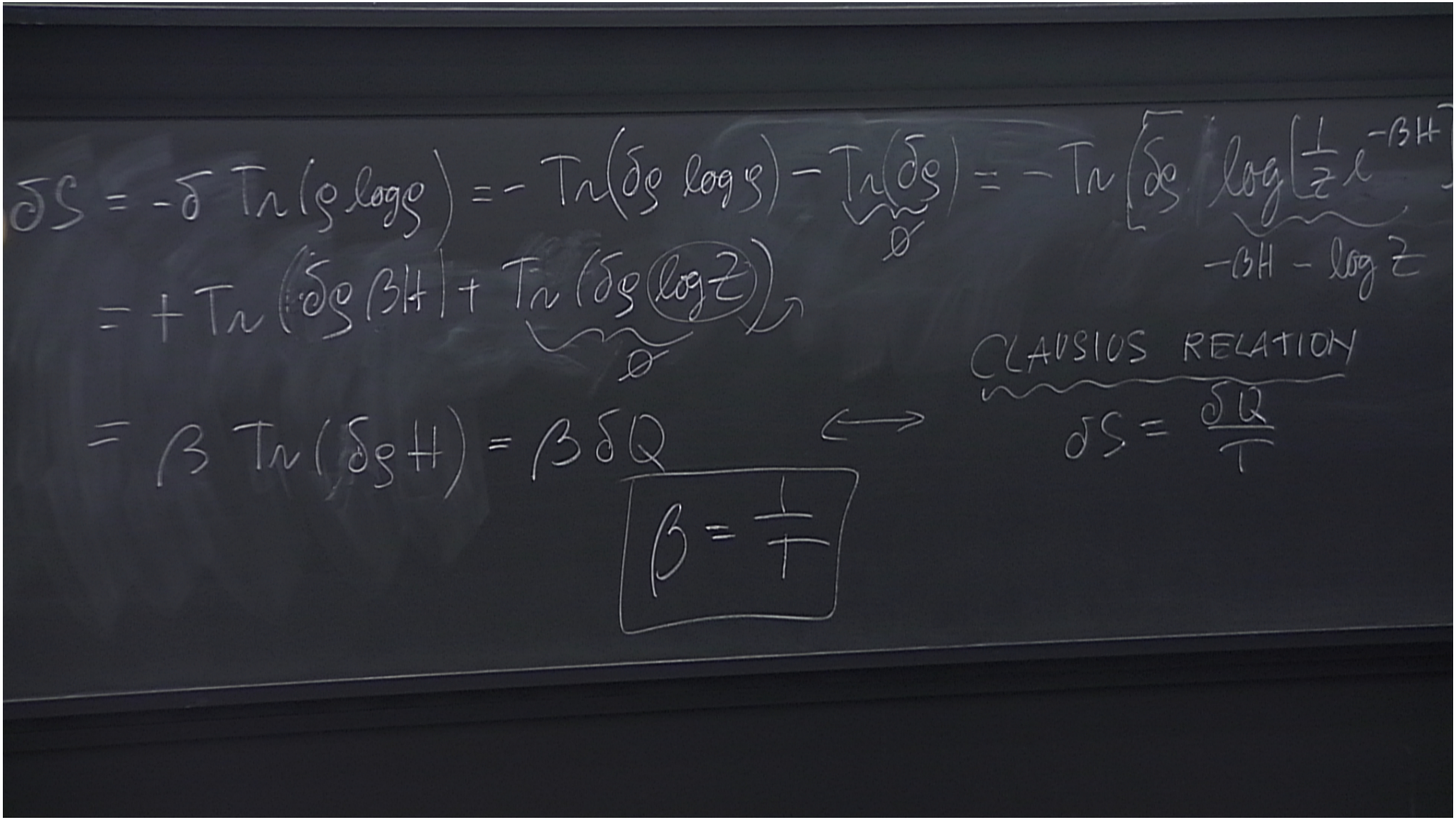
1ST LAW

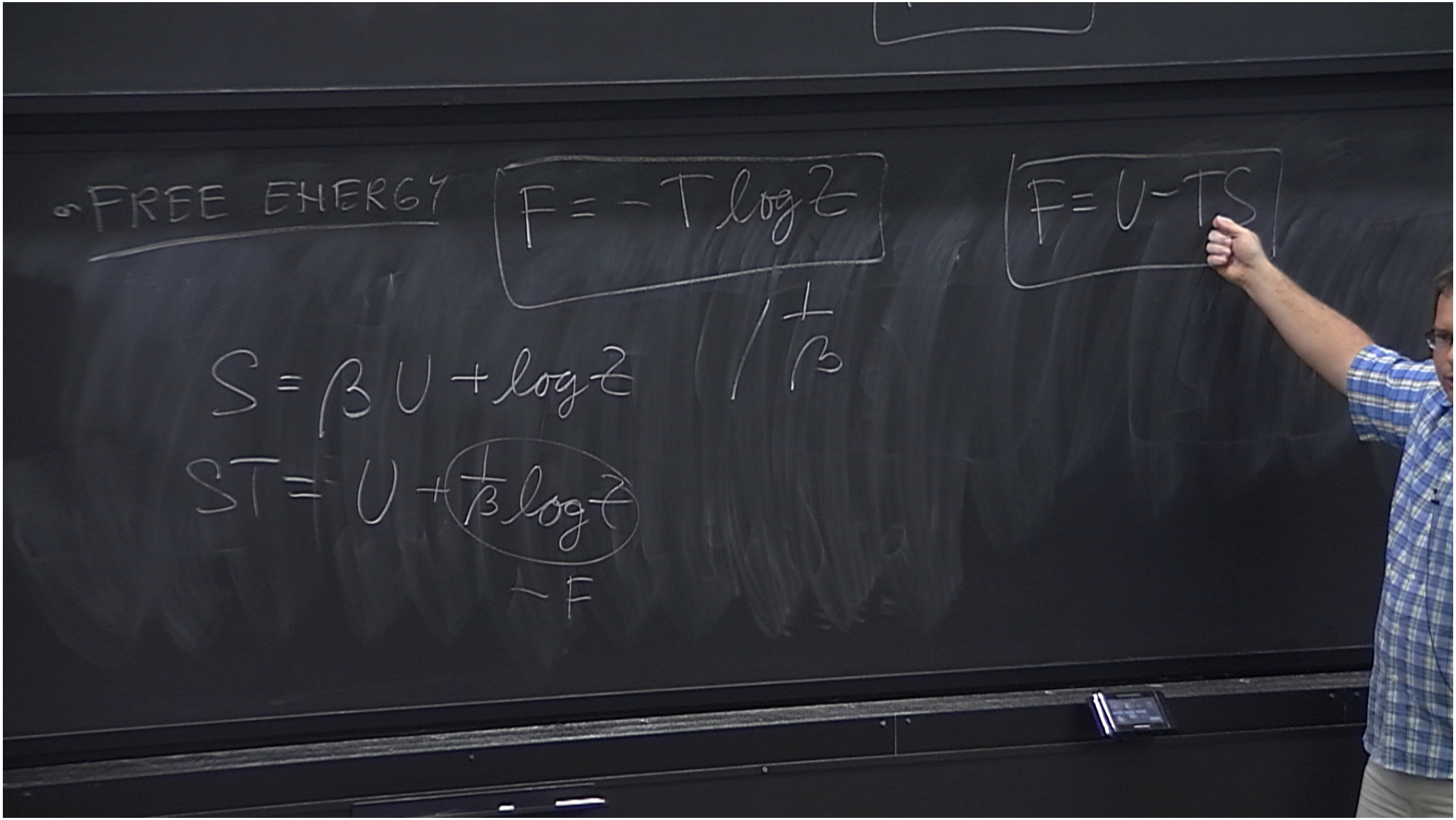
$= \mathrm{Tr}\, \ell^{-\beta H}$

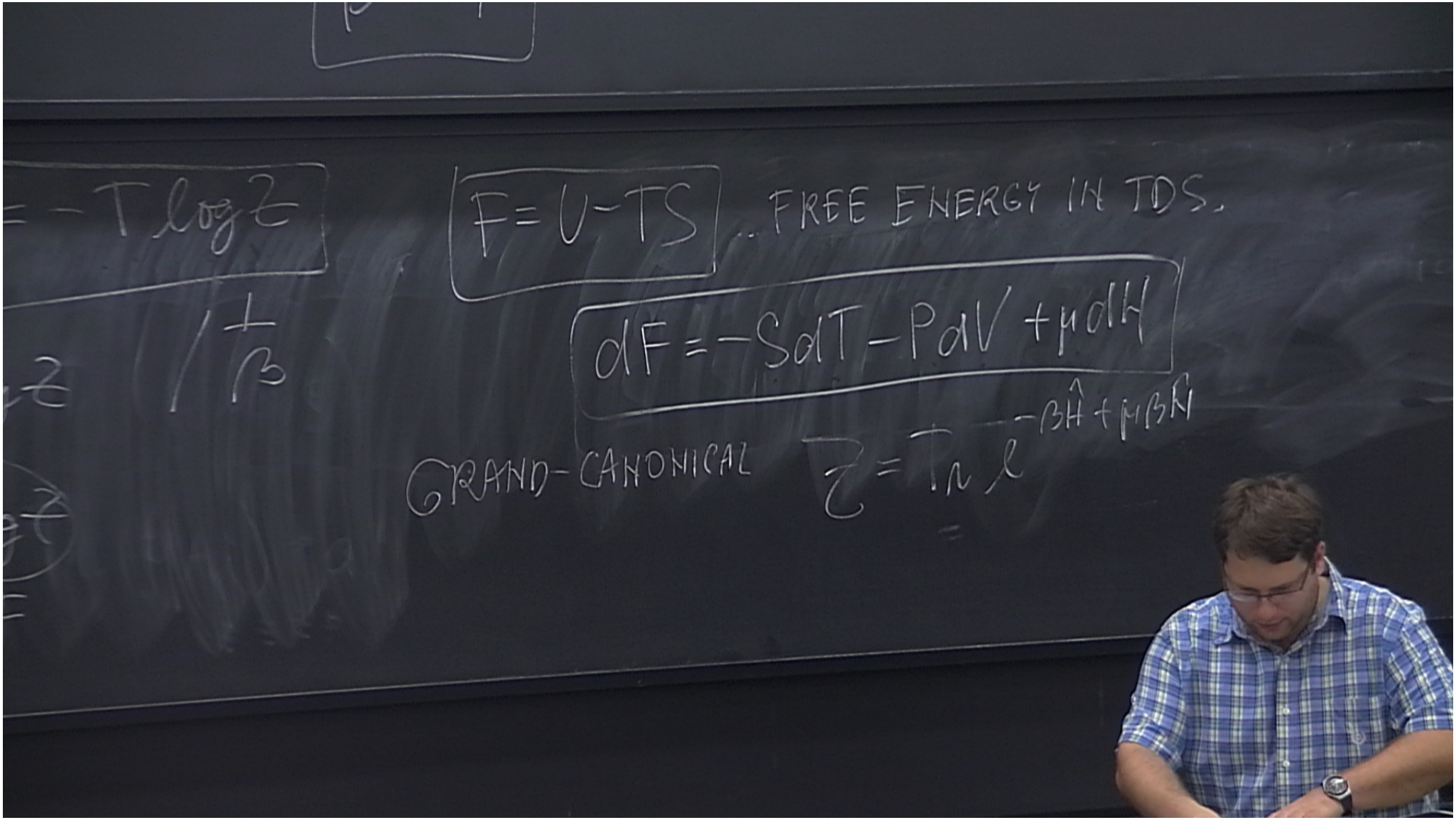



$-\delta \mathrm{Tr}(\rho \log \rho) = -\mathrm{Tr}(\delta\rho \log\rho) - \underbrace{\mathrm{Tr}(\delta\rho)}_{0} = -\mathrm{Tr}\left[\delta\rho \underbrace{\log\left[\frac{1}{Z} e^{-\beta H}\right]}_{-\beta H - \log Z}\right]$


D LAW:
$\delta S = -\delta\, Tr(\rho \log\rho) = -Tr(\delta\rho \log\rho) - Tr(\delta\rho)$
$= +Tr(\delta\rho\, \beta H) + Tr(\delta\rho \log Z)$
$= \beta\, Tr(\delta\rho H)$


$\delta S = -\delta\, \mathrm{Tr}(\rho \log \rho) = -\mathrm{Tr}(\delta\rho \log \rho) - \mathrm{Tr}(\delta\rho)$
$= -\mathrm{Tr}\left[\delta\rho \log\left(\frac{1}{Z} e^{-\beta H}\right)\right]$
$-\beta H - \log Z$
$= +\mathrm{Tr}(\delta\rho\, \beta H) + \mathrm{Tr}(\delta\rho \log Z)$
$= \beta\, \mathrm{Tr}(\delta\rho\, H) = \beta\, \delta Q$
$\beta = \frac{1}{T}$
CLAUSIUS RELATION
$\delta S = \frac{\delta Q}{T}$


FREE ENERGY
$F = -T \log Z$
$F = U - TS$
$S = \beta U + \log Z$
$1/\beta$
$ST = U + \frac{1}{\beta} \log Z$
$\sim F$


$= -T \log Z$
$\frac{1}{\beta}$
$F = U - TS$ .. FREE ENERGY IN TDS.
$dF = -SdT - PdV + \mu dN$
GRAND-CANONICAL
$Z = \sum_N e^{-\beta \hat{H} + \mu \beta N}$