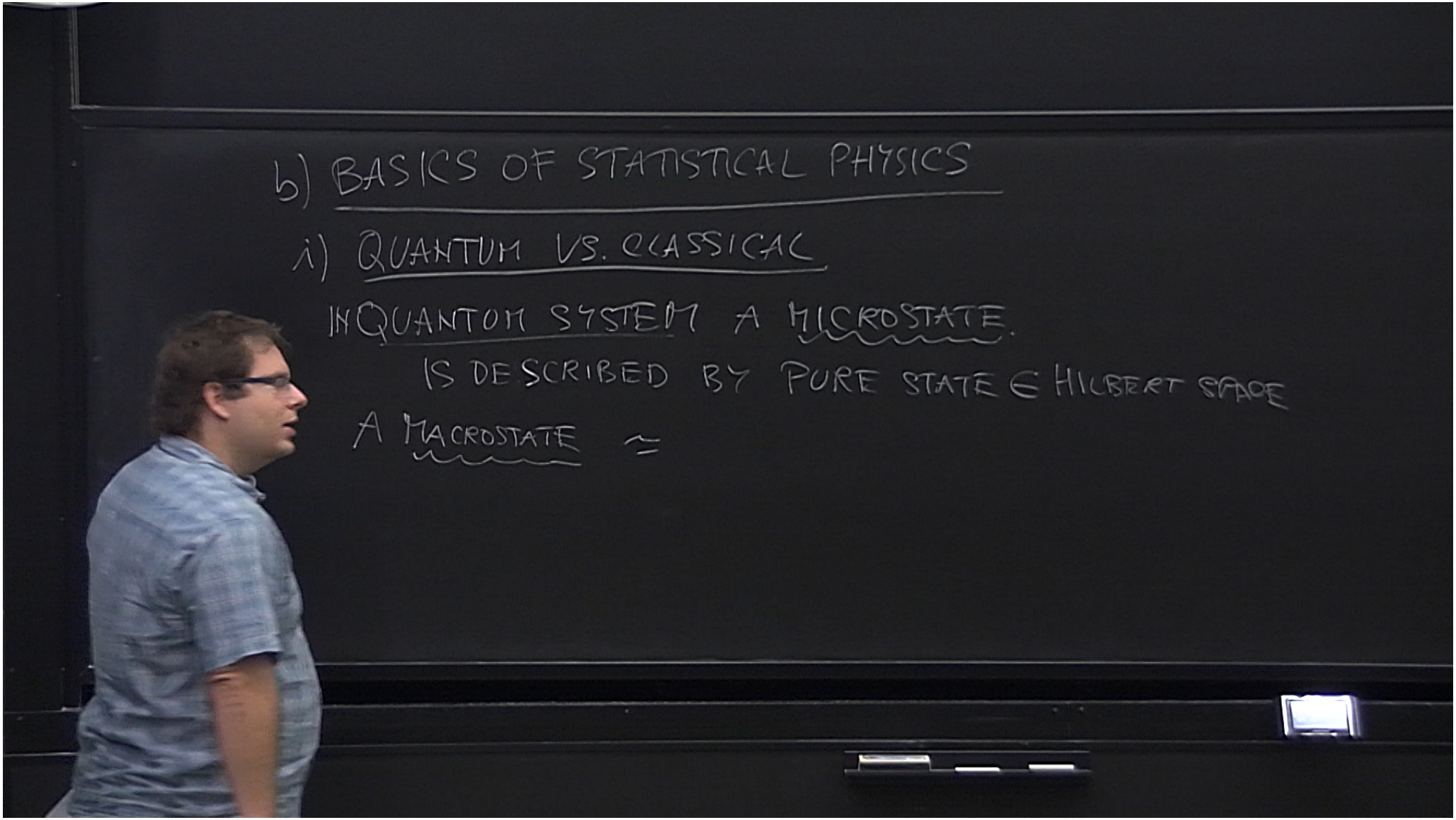
Title: PSI 17/18 - Statistical Mechanics - Lecture 2

Date: Oct 11, 2017 10:45 AM

URL: http://pirsa.org/17100035

Abstract:


b) BASICS OF STATISTICAL PHYSICS
i) QUANTUM VS. CLASSICAL
IN QUANTUM SYSTEM A MICROSTATE
IS DESCRIBED BY PURE STATE ∈ HILBERT SPACE
A MACROSTATE ≃

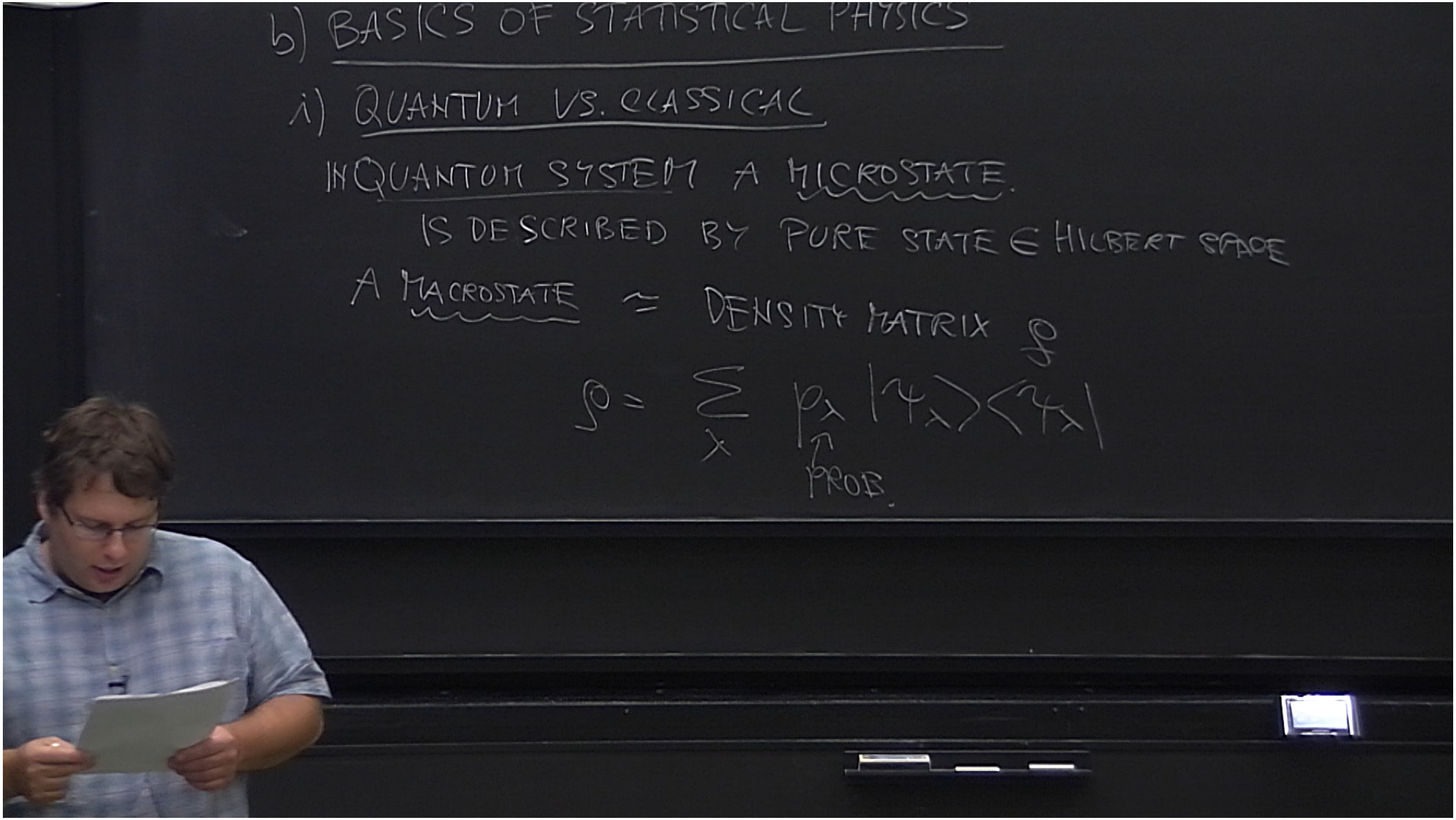
b) BASICS OF STATISTICAL PHYSICS

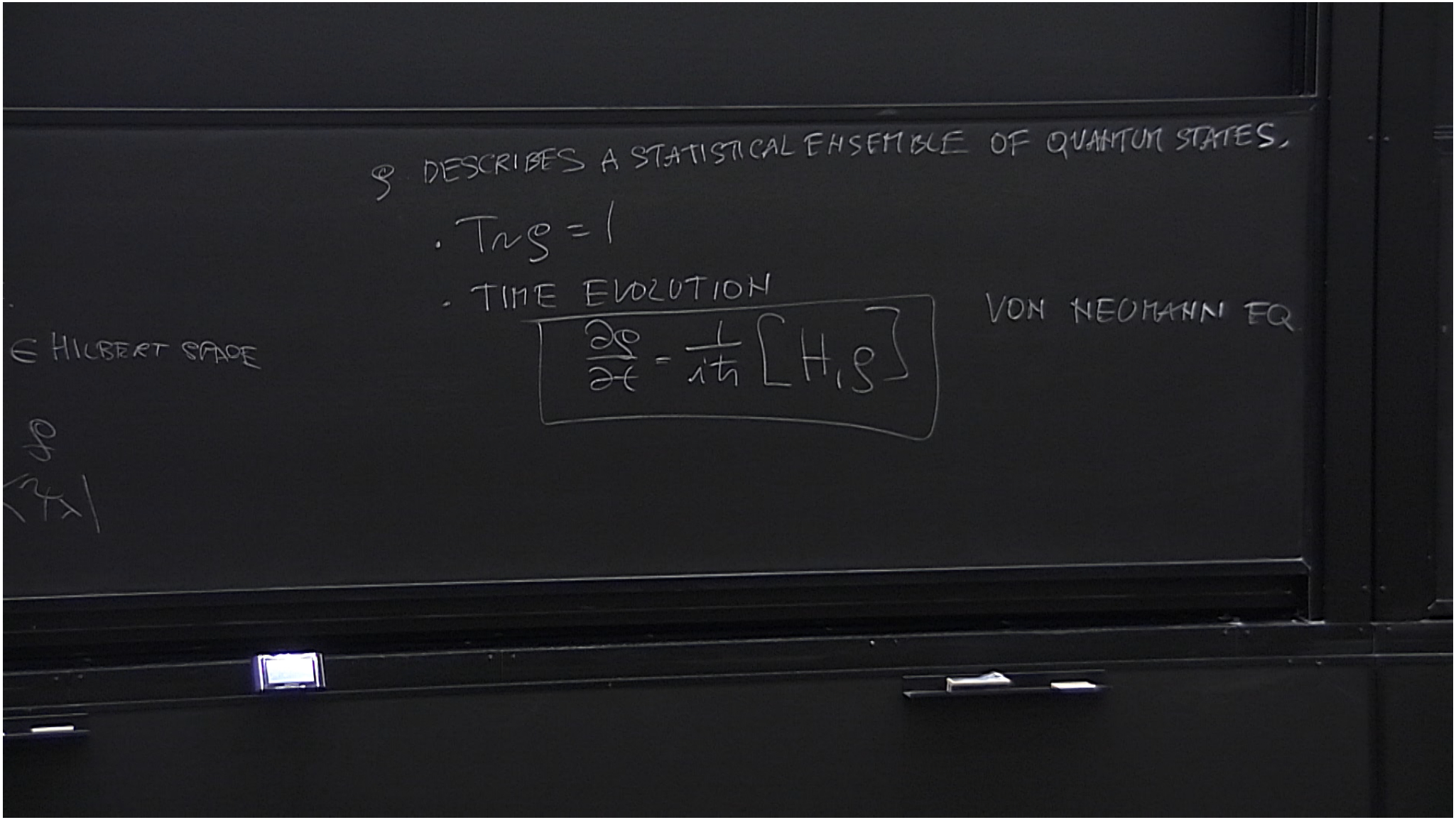
i) QUANTUM VS. CLASSICAL

IN QUANTUM SYSTEM A MICROSTATE
IS DESCRIBED BY PURE STATE $\in$ HILBERT SPACE

A MACROSTATE $\simeq$ DENSITY MATRIX ρ

$\rho =$


b) BASICS OF STATISTICAL PHYSICS
i) QUANTUM VS. CLASSICAL
IN QUANTUM SYSTEM A MICROSTATE
IS DESCRIBED BY PURE STATE ∈ HILBERT SPACE
A MACROSTATE ≃ DENSITY MATRIX ρ
ρ = Σ_x p_x |ψ_x⟩⟨ψ_x|
PROB.


ρ DESCRIBES A STATISTICAL ENSEMBLE OF QUANTUM STATES.
· Tr ρ = 1
· TIME EVOLUTION
$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho]$
VON NEUMANN EQ
∈ HILBERT SPACE

ρ DESCRIBES A STATISTICAL ENSEMBLE OF QUANTUM STATES.

- $\mathrm{Tr}\,\rho = 1$
- TIME EVOLUTION

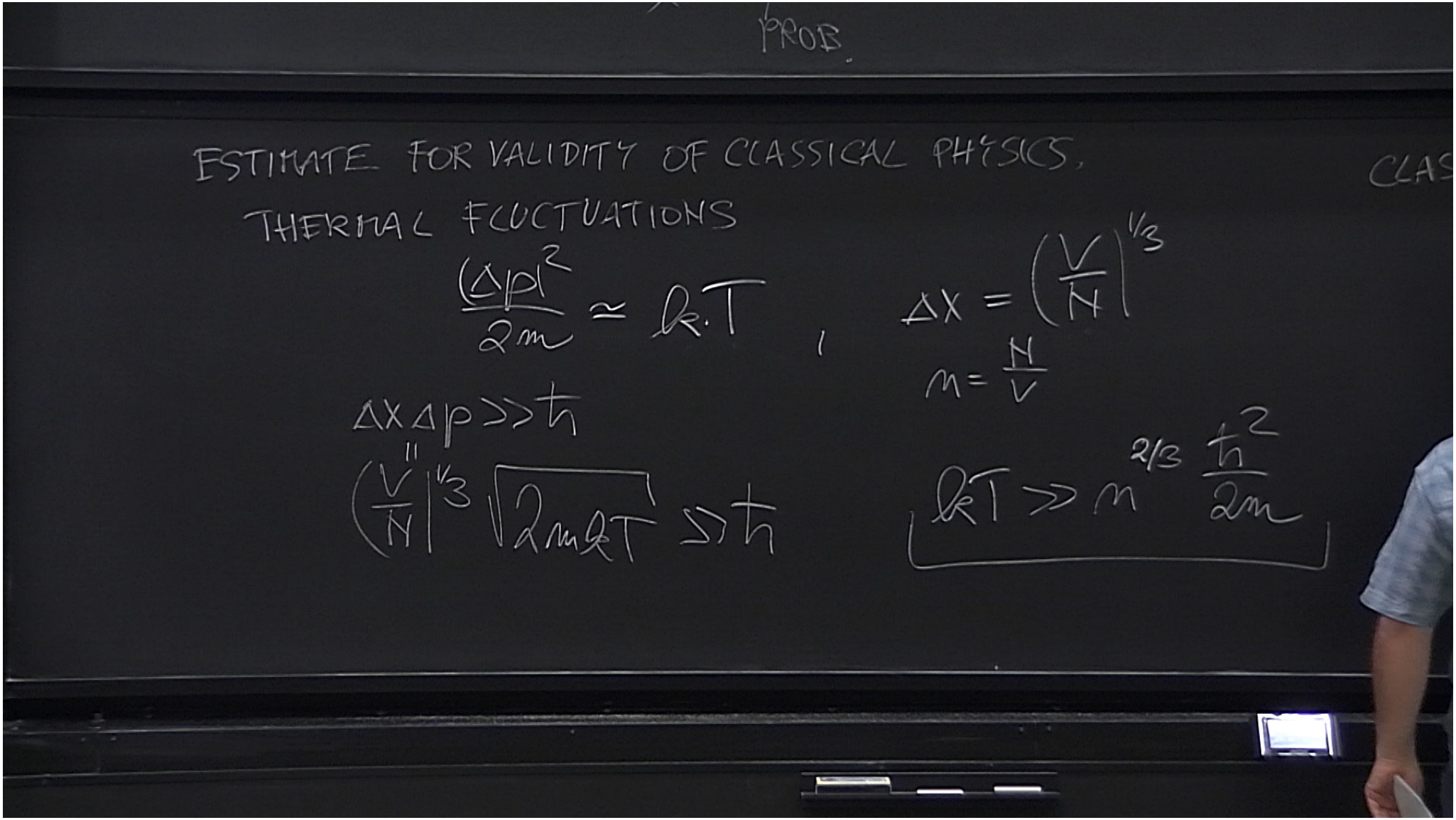
$$\boxed{\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho]}$$

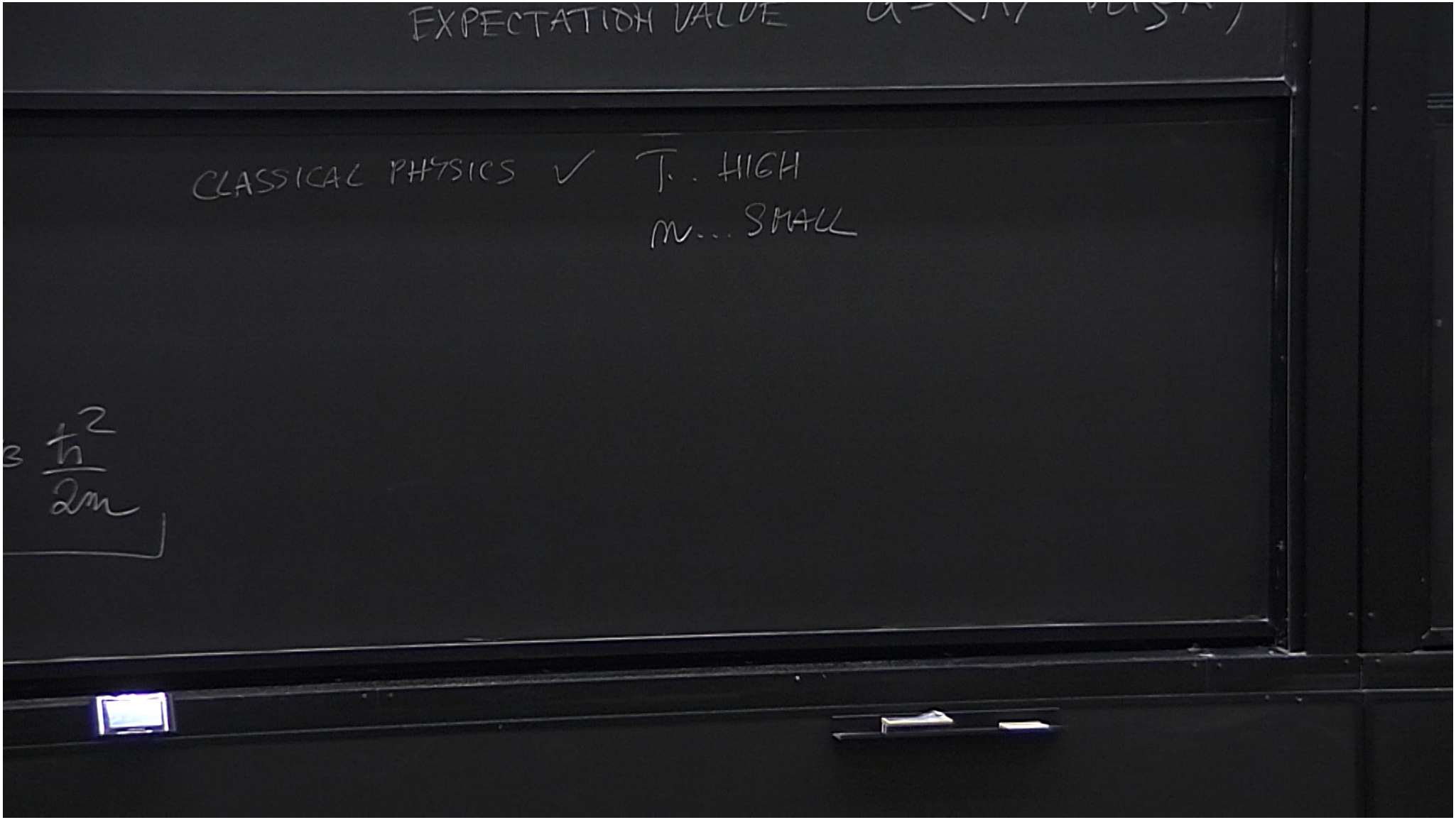
VON NEUMANN EQ.

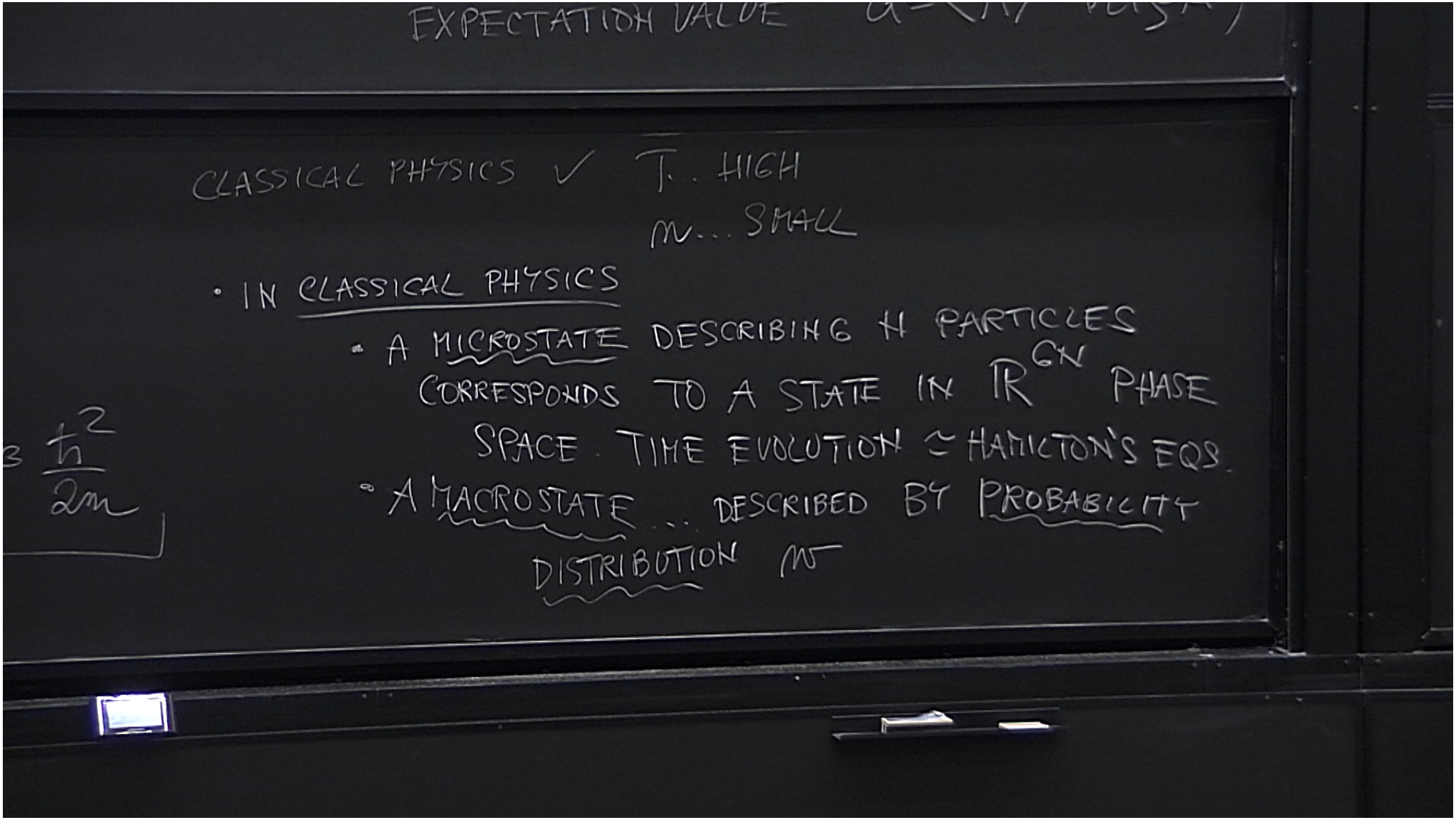
- OBSERVABLE A

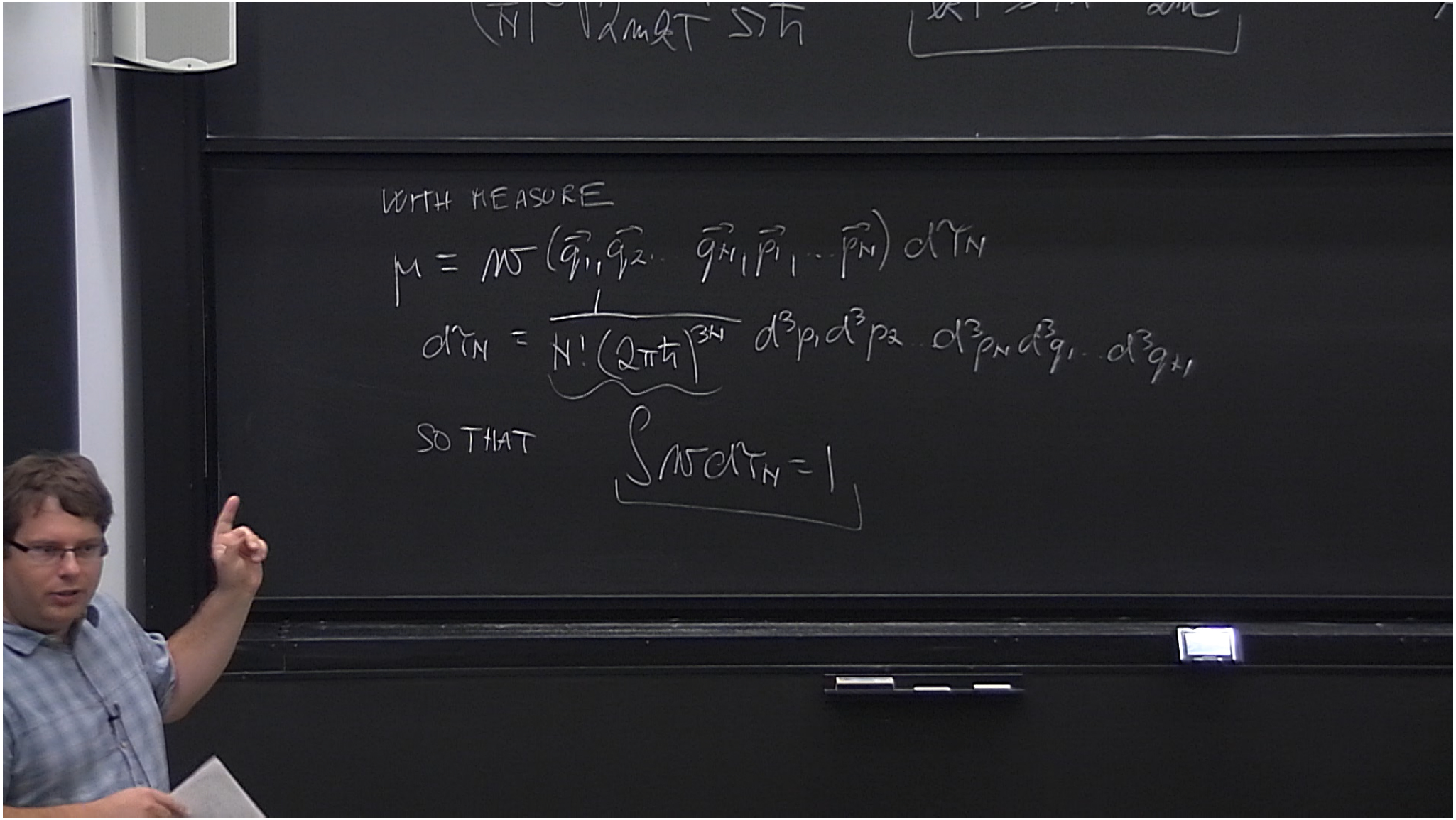
EXPECTATION VALUE $a = \langle A \rangle = \mathrm{Tr}(\rho A)$


PROB.
ESTIMATE FOR VALIDITY OF CLASSICAL PHYSICS.
THERMAL FLUCTUATIONS
$\frac{(\Delta p)^2}{2m} \sim kT$
$\Delta x = \left(\frac{V}{N}\right)^{1/3}$
$n = \frac{N}{V}$
$\Delta x \Delta p \gg \hbar$
$\left(\frac{V}{N}\right)^{1/3}$
$kT \gg n^{2/3} \frac{\hbar^2}{2m}$


PROB.
ESTIMATE FOR VALIDITY OF CLASSICAL PHYSICS.
THERMAL FLUCTUATIONS
$\frac{\langle \Delta p \rangle^2}{2m} \simeq kT$,
$\Delta x = \left(\frac{V}{N}\right)^{1/3}$
$n = \frac{N}{V}$
$\Delta x \Delta p \gg \hbar$
$\left(\frac{V}{N}\right)^{1/3} \sqrt{2mkT} \gg \hbar$
$kT \gg n^{2/3} \frac{\hbar^2}{2m}$


EXPECTATION VALUE
CLASSICAL PHYSICS ✓
T.. HIGH
m... SMALL
$\frac{\hbar^2}{2m}$

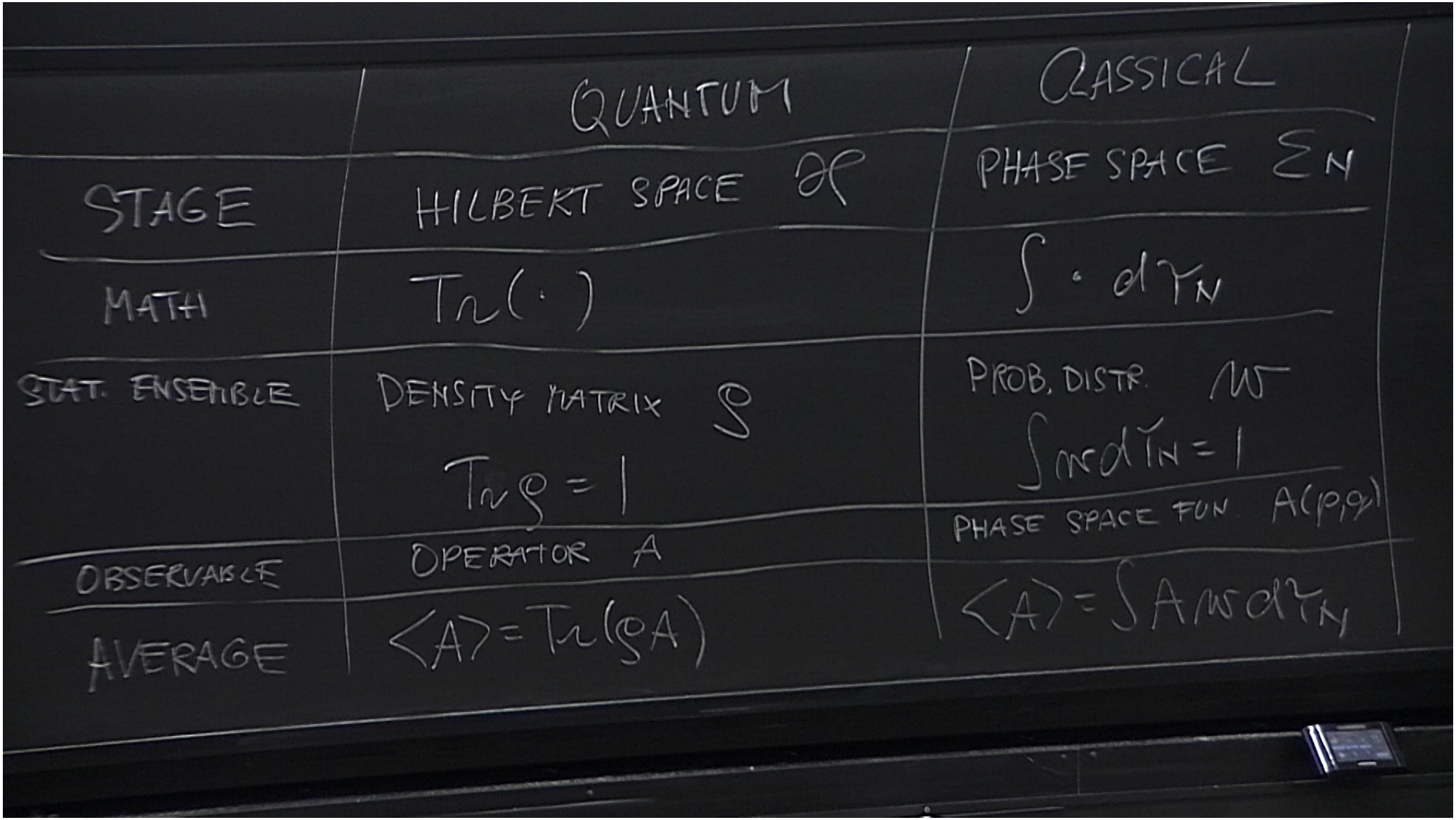

EXPECTATION VALUE
CLASSICAL PHYSICS ✓ T.. HIGH
N... SMALL
• IN CLASSICAL PHYSICS
- A MICROSTATE DESCRIBING N PARTICLES CORRESPONDS TO A STATE IN $\mathbb{R}^{6N}$ PHASE SPACE. TIME EVOLUTION ≃ HAMILTON'S EQS.
- A MACROSTATE ... DESCRIBED BY PROBABILITY DISTRIBUTION
$\frac{\hbar^2}{2m}$

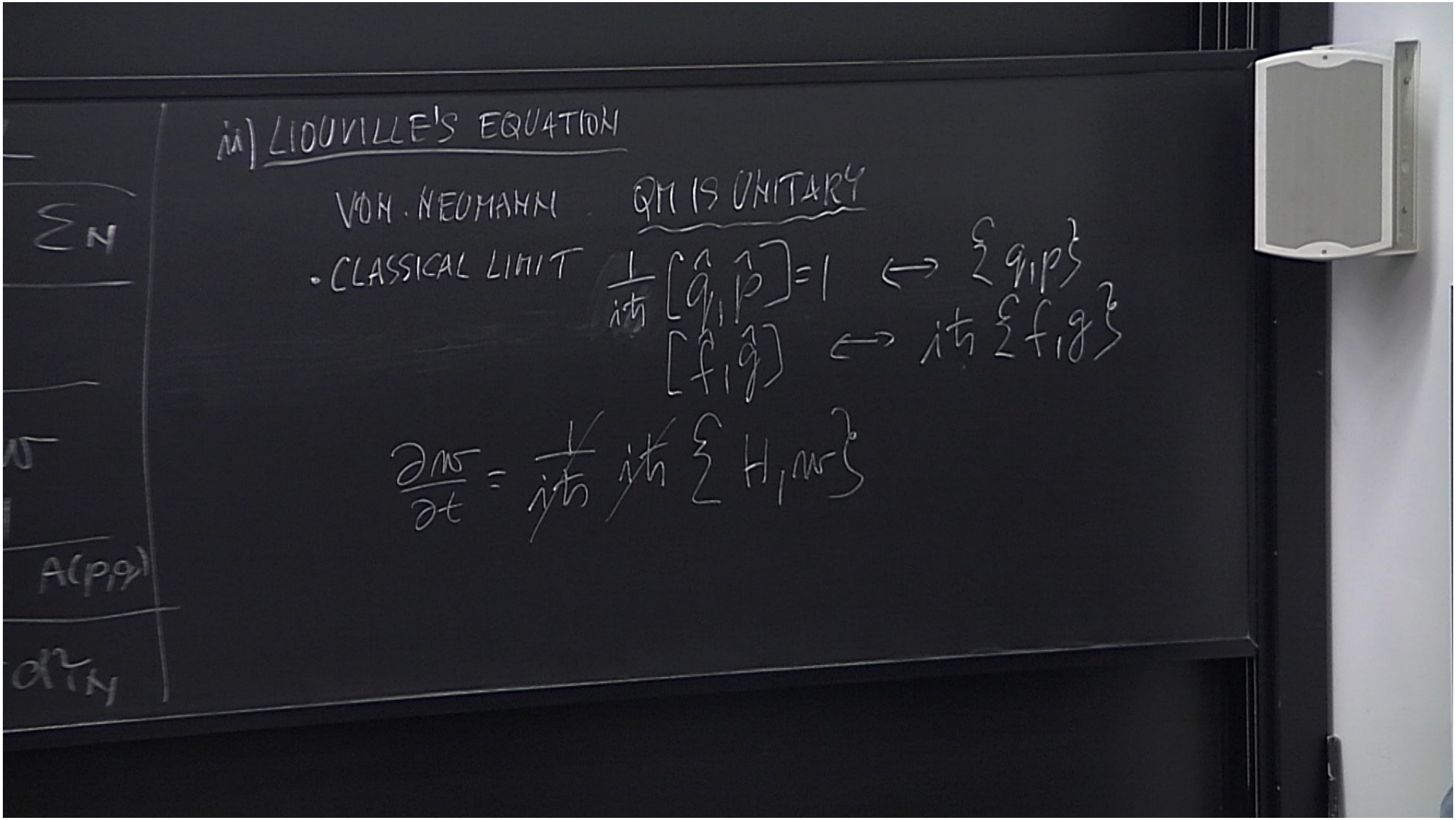

WITH MEASURE
$\mu = \rho_N(\vec{q}_1, \vec{q}_2 \ldots \vec{q}_N, \vec{p}_1 \ldots \vec{p}_N)\, d\Gamma_N$
$d\Gamma_N = \frac{1}{N!(2\pi\hbar)^{3N}} d^3p_1 d^3p_2 \ldots d^3p_N d^3q_1 \ldots d^3q_N$
SO THAT
$\int \rho_N d\Gamma_N = 1$

DISTRIBUTION ρ ON PHASE SPACE

- STATISTICAL ENSEMBLE = HAVING A LARGE NUMBER OF BOXES WITH A GIVEN MACROSTATE. IF RANDOMLY OPEN 1 BOX I FIND A MICROSTATE WITH PROB ρ.
- OBSERVABLE $A(p,q)$

AVERAGE VALUE $\langle A \rangle = \int A(p,q)\, \rho(p,q,t)\, d^{2N}$


QUANTUM
CLASSICAL
STAGE
HILBERT SPACE $\mathcal{H}$
PHASE SPACE Σ_N
MATH
$\mathrm{Tr}(\cdot)$
$\int \cdot \, d\Gamma_N$
STAT. ENSEMBLE
DENSITY MATRIX ρ
$\mathrm{Tr}\rho = 1$
PROB. DISTR. μ
$\int \mu \, d\Gamma_N = 1$
OBSERVABLE
OPERATOR A
PHASE SPACE FUN $A(p,q)$
AVERAGE
$\langle A \rangle = \mathrm{Tr}(\rho A)$
$\langle A \rangle = \int A \mu \, d\Gamma_N$


iii) LIOUVILLE'S EQUATION
VON. NEUMANN
QM IS UNITARY
• CLASSICAL LIMIT
$\frac{1}{i\hbar}[\hat{q},\hat{p}]=1 \leftrightarrow \{q,p\}$
$[\hat{f},\hat{g}] \leftrightarrow i\hbar\{f,g\}$
$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar} i\hbar \{H,\rho\}$
Σ_N
$A(p,q)$
$d^2\Gamma_N$

[iii] LIOUVILLE'S EQUATION

VON NEUMANN — QM IS UNITARY

- CLASSICAL LIMIT

$$\frac{1}{i\hbar}[\hat{q},\hat{p}] = 1 \longleftrightarrow \{q,p\}$$

$$[f,g] \longleftrightarrow i\hbar\{f,g\}$$

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar} i\hbar \{H,\rho\}$$

$$\therefore \boxed{\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0}$$

LIOUVILLE'S EQ.

CONSEQUENCE FOR STAT PHYS.

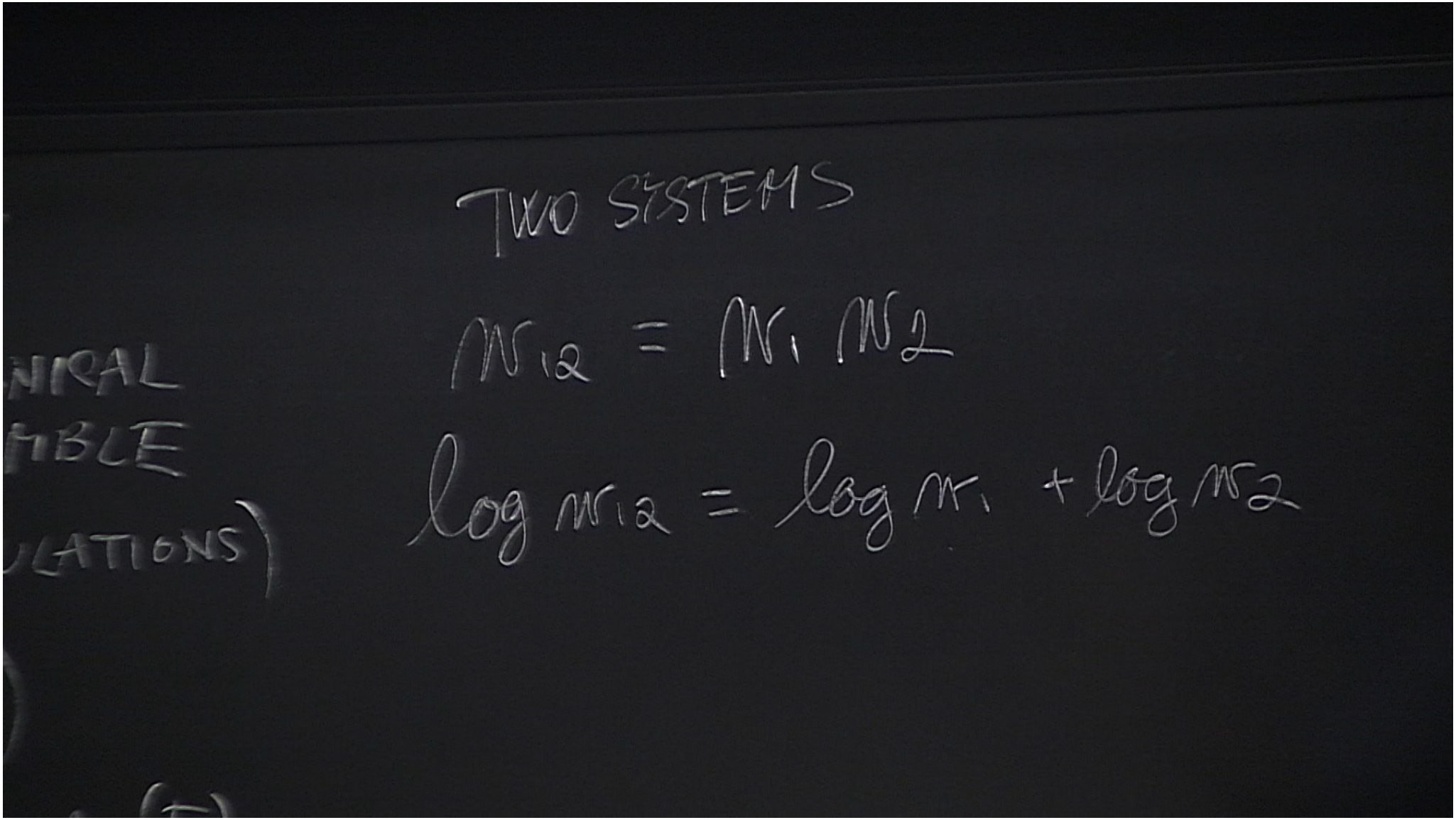
- $\Gamma = \text{CONST}$ ... MICROCANONICAL ENSEMBLE

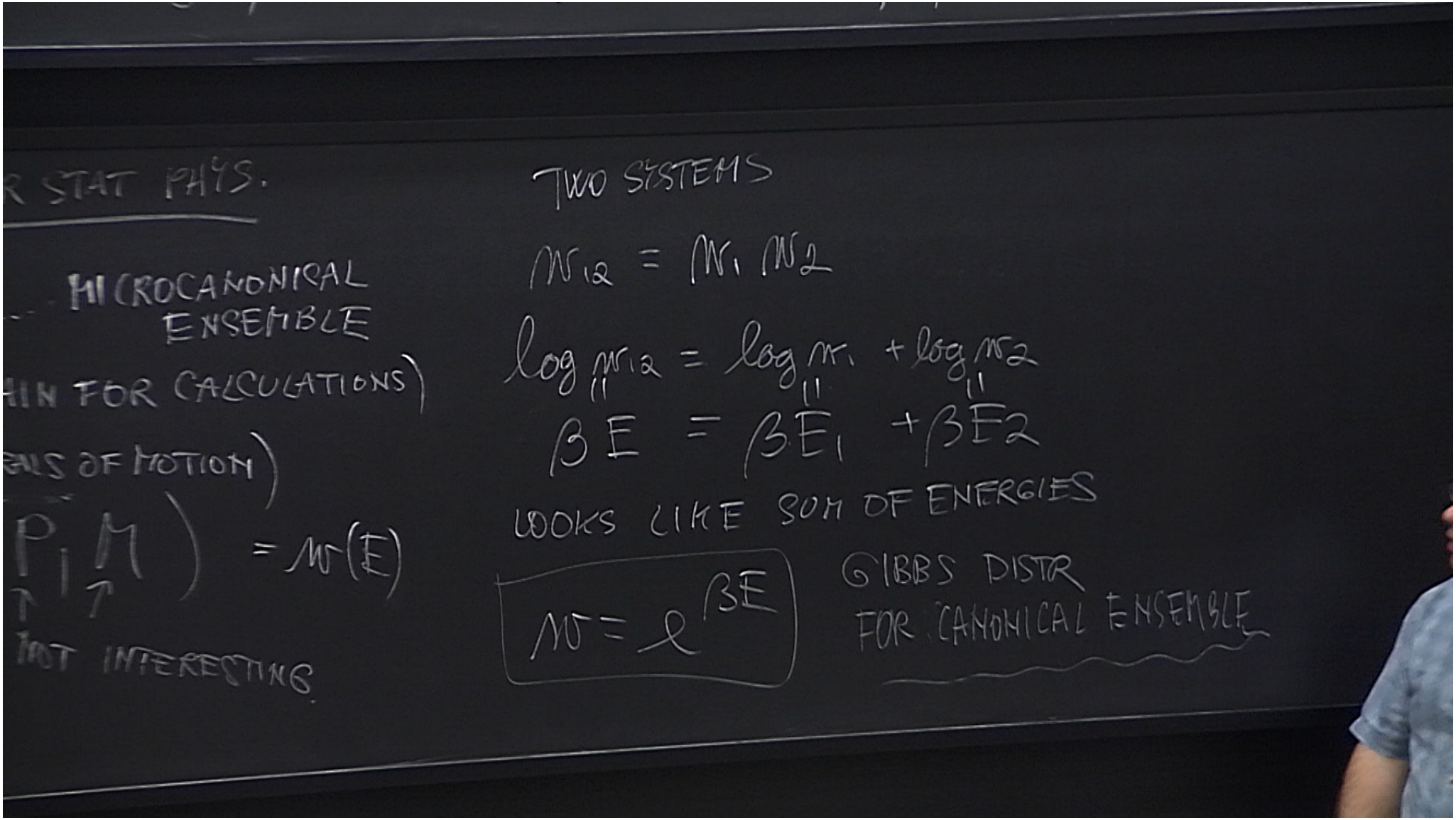
  (PAIN FOR CALCULATIONS)

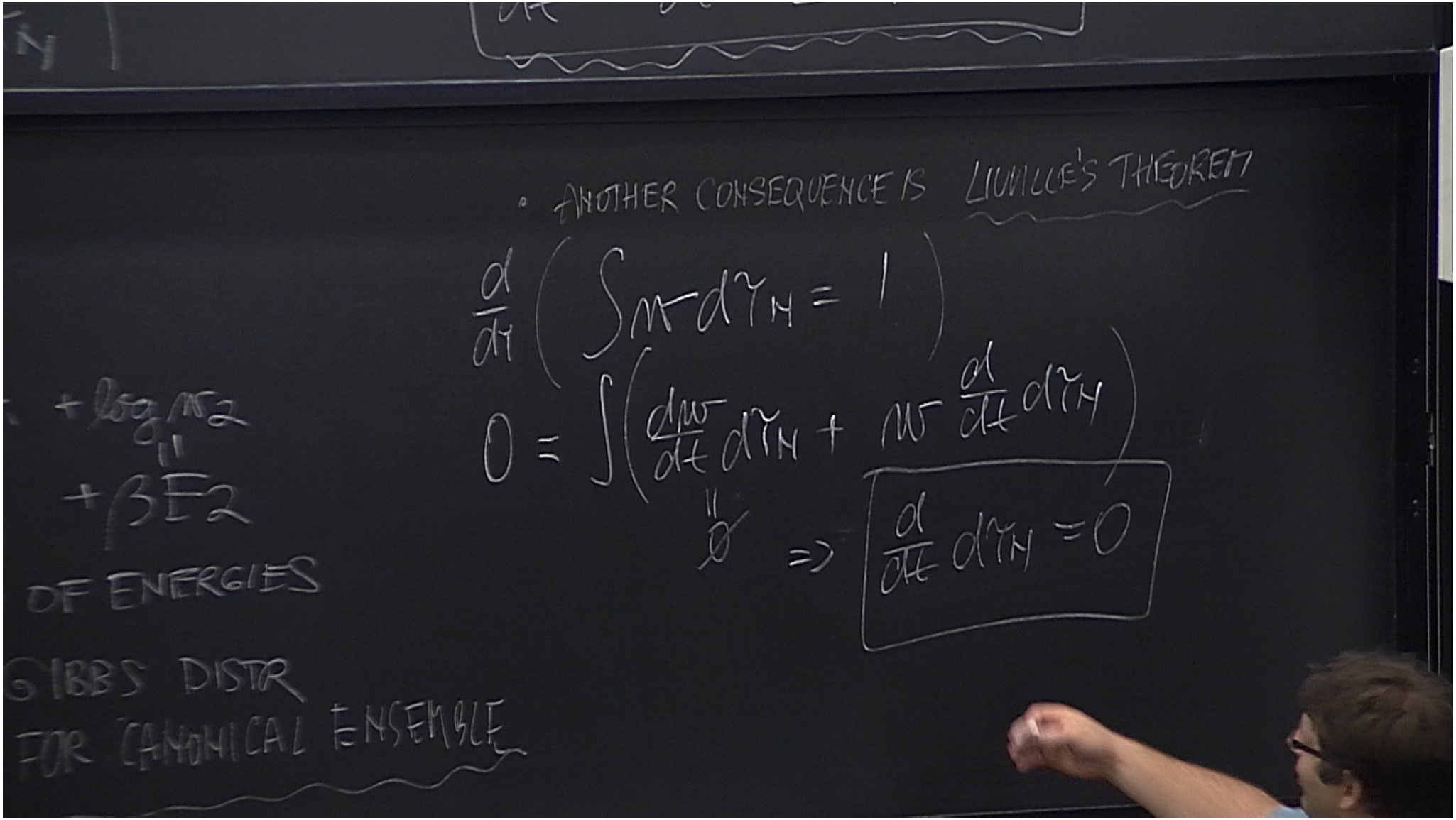
- $\Gamma = \Gamma(\text{INTEGRALS OF MOTION})$

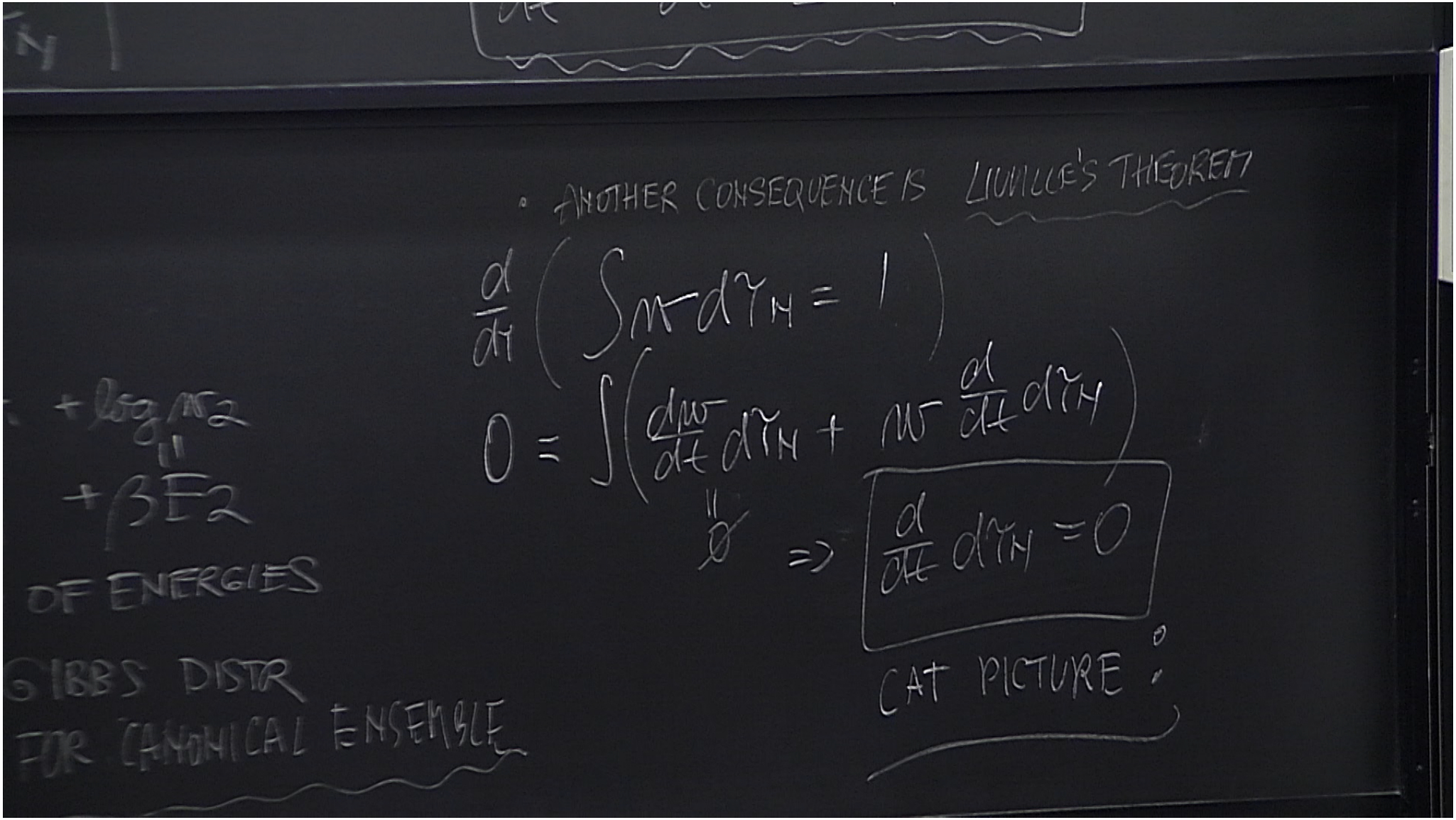
  $= \Gamma(E, P, M) = \Gamma(E)$

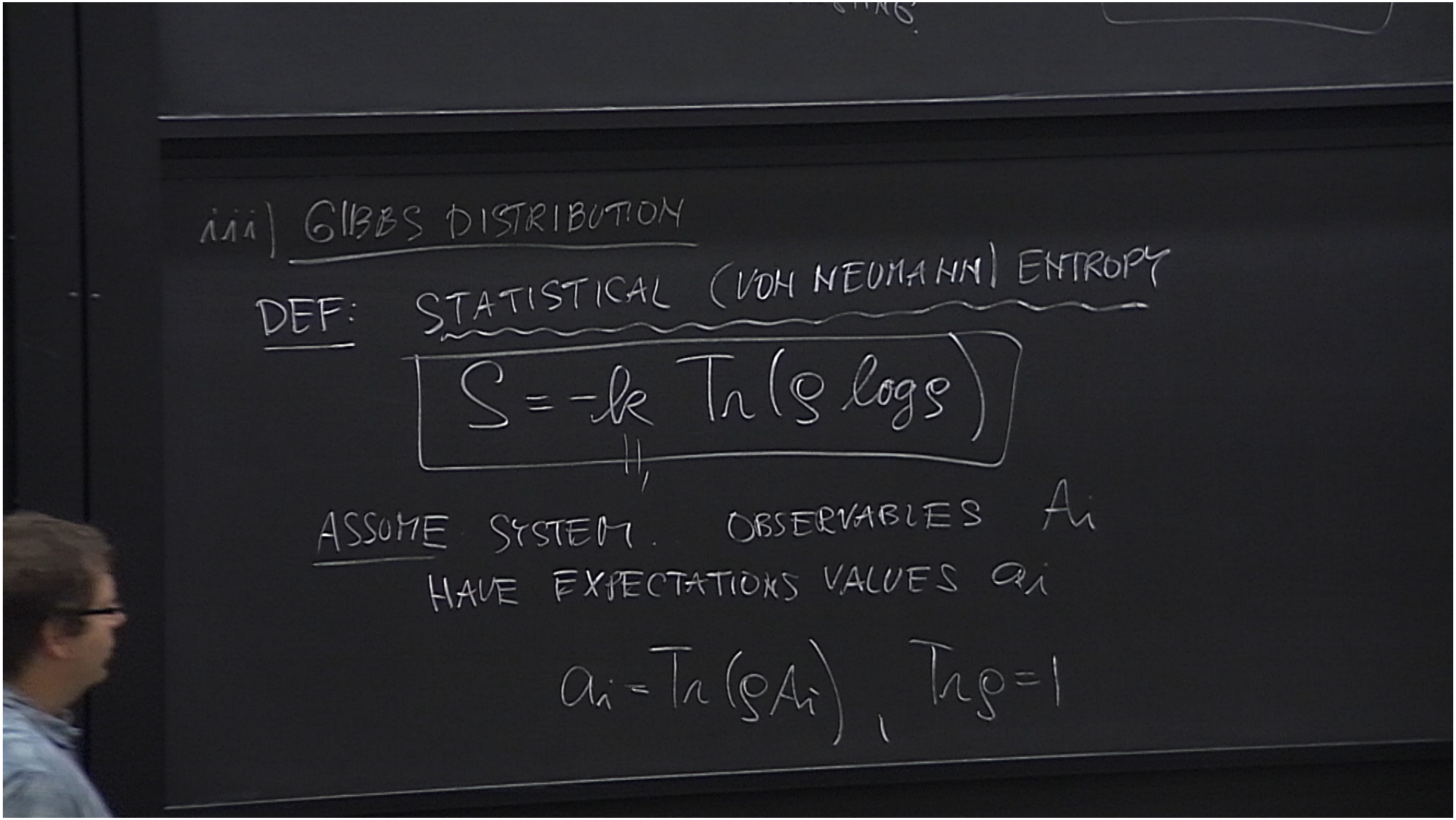
  ↑ NOT INTERESTING ↑


TWO SYSTEMS
$N_{12} = N_1 N_2$
$\log N_{12} = \log N_1 + \log N_2$


R STAT PHYS.
MICROCANONICAL ENSEMBLE
HIN FOR CALCULATIONS)
ALS OF MOTION)
$(P_i M) = \Omega(E)$
NOT INTERESTING
TWO SYSTEMS
$\Omega_{12} = \Omega_1 \Omega_2$
$\log \Omega_{12} = \log \Omega_1 + \log \Omega_2$
$\beta E = \beta E_1 + \beta E_2$
LOOKS LIKE SUM OF ENERGIES
$\Omega = e^{\beta E}$
GIBBS DISTR FOR CANONICAL ENSEMBLE


• ANOTHER CONSEQUENCE IS LIOUVILLE'S THEOREM
$\frac{d}{dt}\left(\int \rho_N \, d\Gamma_N = 1\right)$
$0 = \int \left(\frac{d\rho}{dt} d\Gamma_N + \rho \frac{d}{dt} d\Gamma_N\right)$
$\frac{d}{dt} d\Gamma_N = 0$
$+\beta E_2$
OF ENERGIES
GIBBS DISTR
FOR CANONICAL ENSEMBLE


ANOTHER CONSEQUENCE IS LIOUVILLE'S THEOREM
$\frac{d}{dt}\left(\int \rho_N \, d\Gamma_N = 1\right)$
$0 = \int \left(\frac{d\rho}{dt} d\Gamma_N + \rho \frac{d}{dt} d\Gamma_N\right)$
$\frac{d}{dt} d\Gamma_N = 0$
CAT PICTURE
$+\beta E_2$
OF ENERGIES
GIBBS DISTR
FOR CANONICAL ENSEMBLE

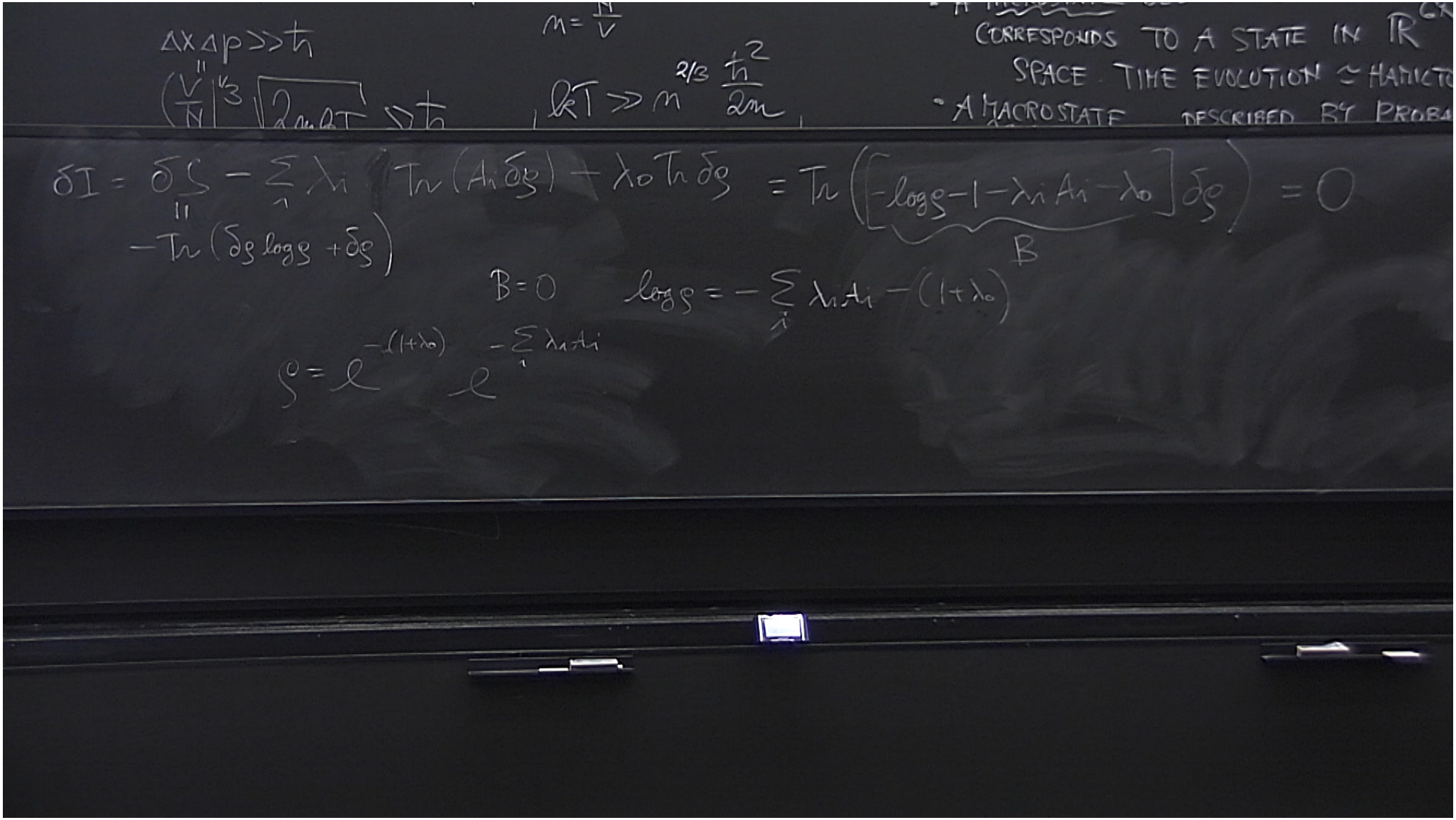

iii) GIBBS DISTRIBUTION
DEF: STATISTICAL (VON NEUMANN) ENTROPY
$S = -k\,\mathrm{Tr}(\rho \log \rho)$
ASSUME SYSTEM. OBSERVABLES A_i
HAVE EXPECTATIONS VALUES a_i
$a_i = \mathrm{Tr}(\rho A_i)$, $\mathrm{Tr}\rho = 1$

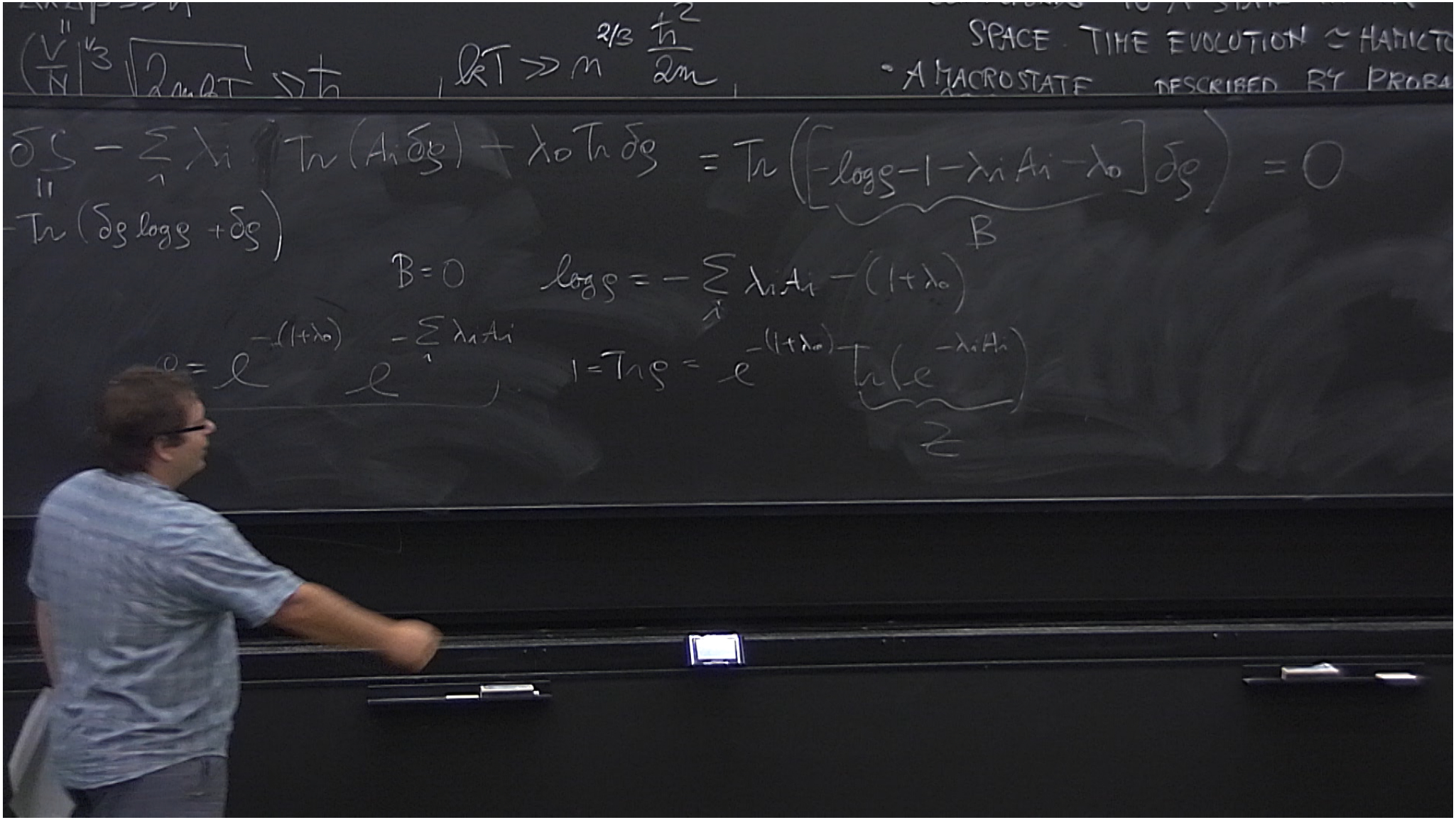
PRINCIPLE OF MAXIMAL MESS: THE DENSITY MATRIX ρ REPRESENTING THE EQUILIBRIUM STATE OF A MICROSYSTEM IS SUCH THAT IT MAXIMIZES THE STAT. ENTROPY, PROVIDED THE (MACROSCOPICAL) CONSTRAINTS

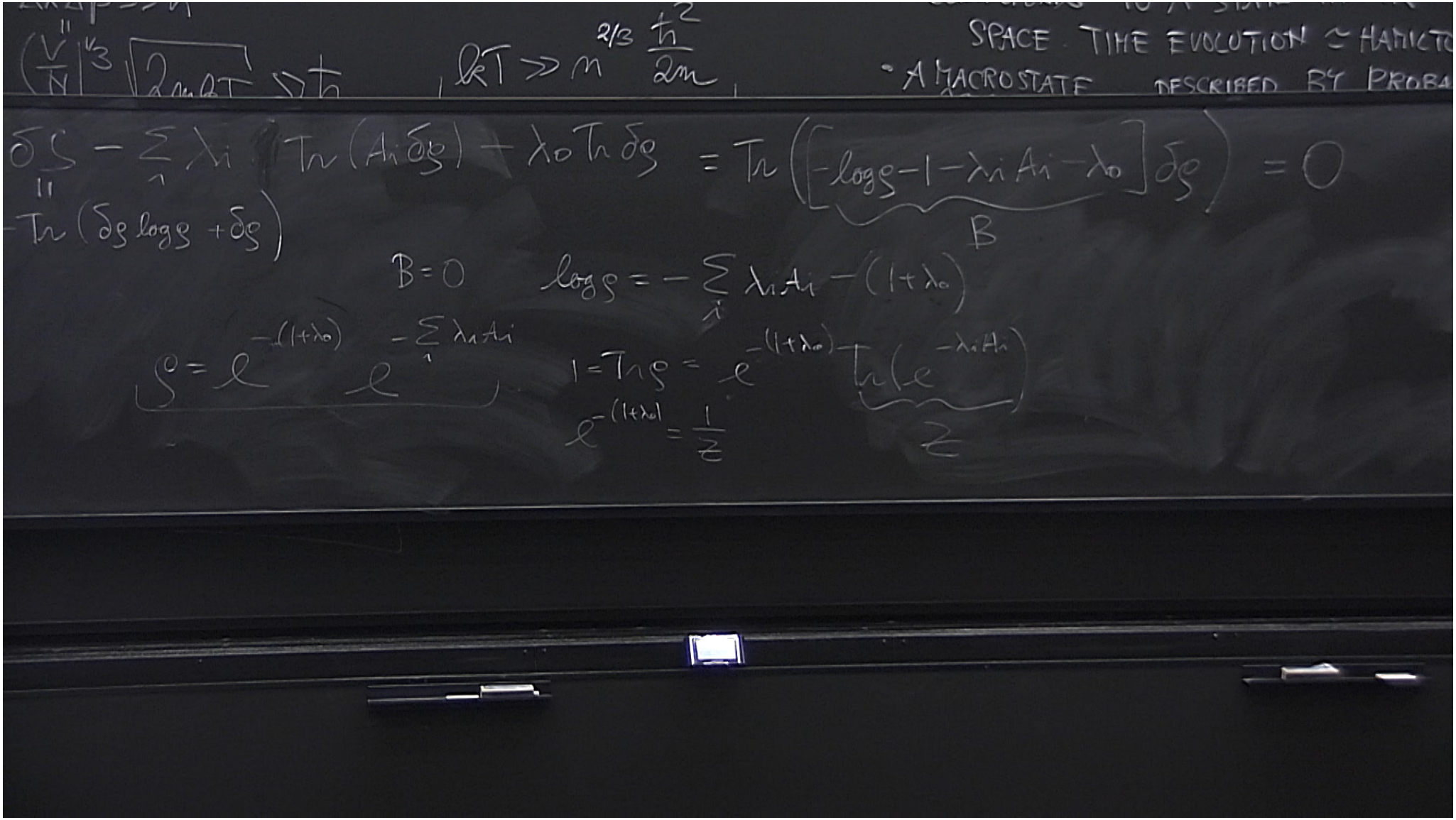


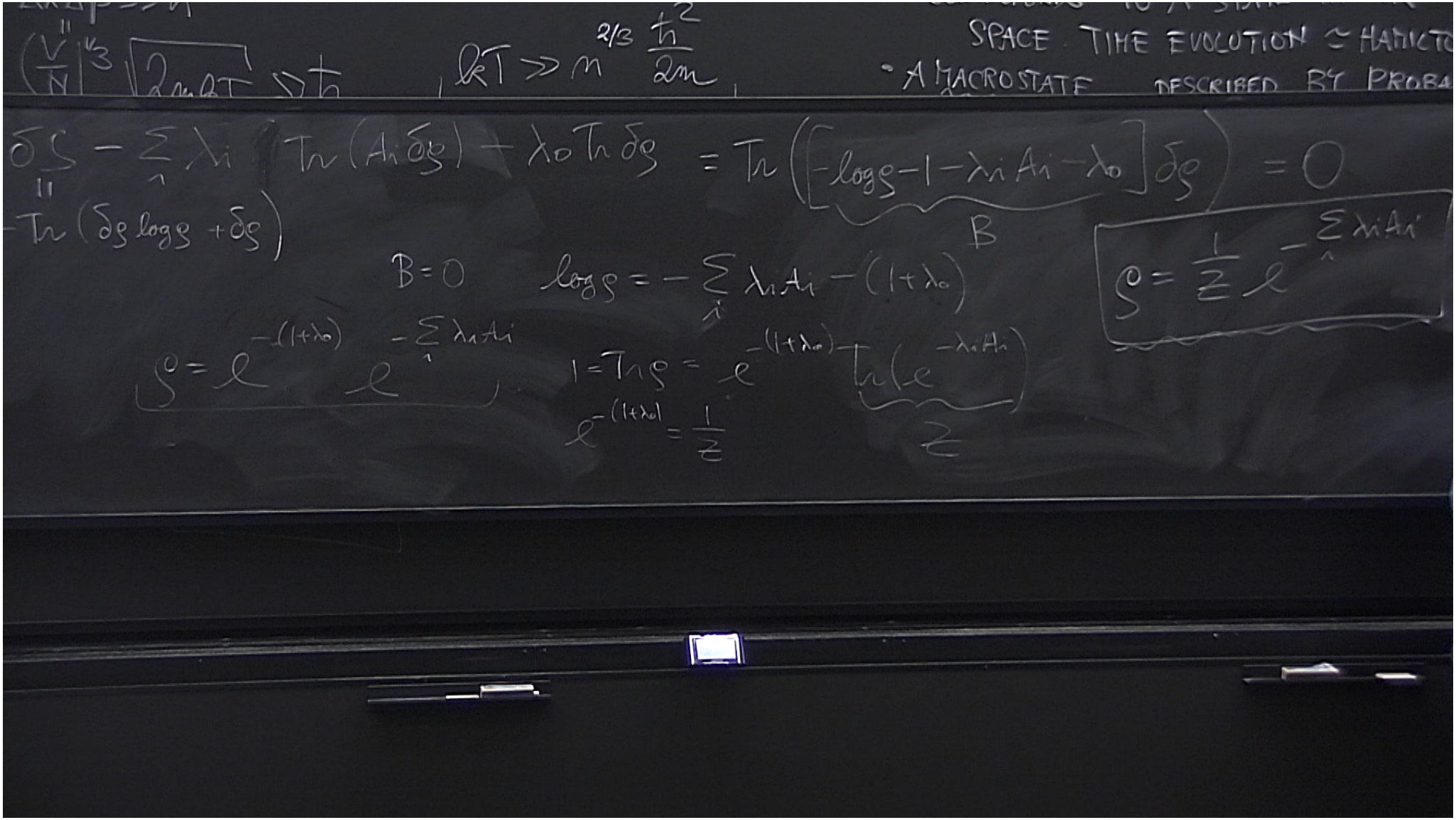
PRINCIPLE OF MAXIMAL MESS: THE DENSITY MATRIX ρ REPRESENTING THE EQUILIBRIUM STATE OF A MICROSYSTEM IS SUCH THAT IT MAXIMIZES THE STAT. ENTROPY, PROVIDED THE (MACROSCOPICAL) CONSTRAINTS

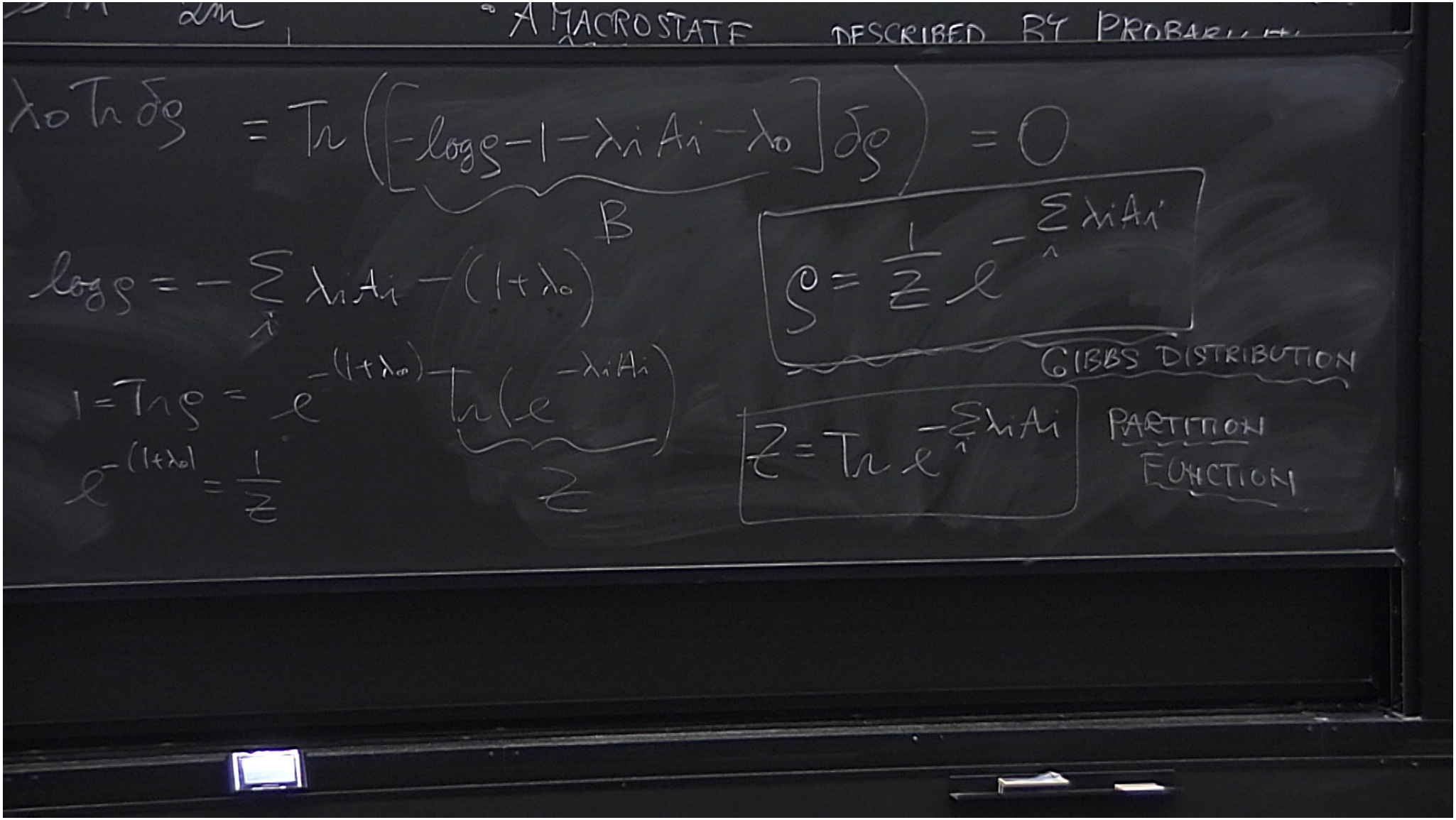
WANT TO EXTREMIZE $I = S - \sum_i \lambda_i \left(\mathrm{Tr}(\rho A_i) - a_i \right) - \lambda_0 \left(\mathrm{Tr}\rho - 1 \right)$


$\Delta x \Delta p \gg \hbar$
$n = \frac{N}{V}$
$\left(\frac{V}{N}\right)^{1/3} \sqrt{2mkT} \gg \hbar$
$kT \gg n^{2/3} \frac{\hbar^2}{2m}$
CORRESPONDS TO A STATE IN $\mathbb{R}^{6N}$
SPACE. TIME EVOLUTION ≅ HAMILTO
A MACROSTATE DESCRIBED BY PROBA
$\delta I = \delta S - \sum_i \lambda_i \left(\mathrm{Tr}(A_i \delta\rho) + \lambda_0 \mathrm{Tr}\,\delta\rho \right) = \mathrm{Tr}\left(\left[-\log\rho - 1 - \lambda_i A_i - \lambda_0 \right] \delta\rho \right) = 0$
$S = -\mathrm{Tr}(\rho \log\rho + \rho)$
B
$B = 0 \quad \log\rho = -\sum_i \lambda_i A_i - (1+\lambda_0)$
$\rho = e^{-(1+\lambda_0)} \; e^{-\sum_i \lambda_i A_i}$


SPACE. TIME EVOLUTION ≃ HAMILTO
A MACROSTATE DESCRIBED BY PROBA
B=0
B
Z


SPACE. TIME EVOLUTION ≃ HAMILTO
A MACROSTATE DESCRIBED BY PROBA
B=0
Z


SPACE TIME EVOLUTION ≃ HAMILTO
A MACROSTATE DESCRIBED BY PROBA
$\delta S = -\sum_i \lambda_i \left(\mathrm{Tr}(A_i \delta\rho) + \lambda_0 \mathrm{Tr}\,\delta\rho \right) = \mathrm{Tr}\left(\left[-\log\rho - 1 - \lambda_i A_i - \lambda_0 \right] \delta\rho \right) = 0$
$-\mathrm{Tr}(\delta\rho \log\rho + \delta\rho)$
B
$B = 0 \qquad \log\rho = -\sum_i \lambda_i A_i - (1+\lambda_0)$
$\rho = \frac{1}{Z} e^{-\sum \lambda_i A_i}$
$\rho = e^{-(1+\lambda_0)} e^{-\sum \lambda_i A_i}$
$1 = \mathrm{Tr}\,\rho = e^{-(1+\lambda_0)} \mathrm{Tr}\left(e^{-\lambda_i A_i} \right)$
Z
$e^{-(1+\lambda_0)} = \frac{1}{Z}$

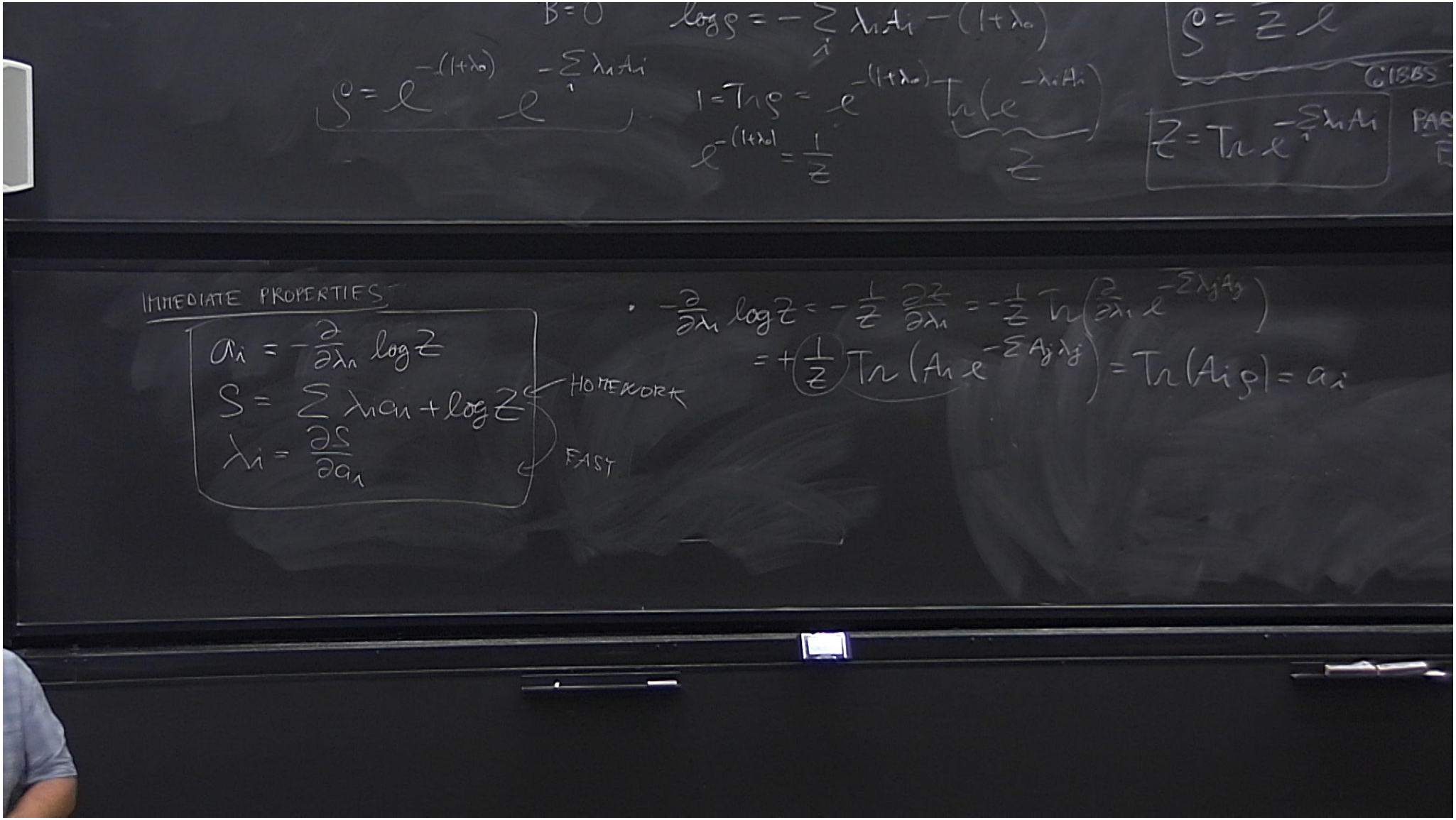

A MACROSTATE DESCRIBED BY PROBABILITY
$\lambda_0 \mathrm{Tr}\,\delta\rho = \mathrm{Tr}\left(\left[-\log\rho - 1 - \lambda_i A_i - \lambda_0\right]\delta\rho\right) = 0$
B
$\log\rho = -\sum_i \lambda_i A_i - (1+\lambda_0)$
$\rho = \frac{1}{Z} e^{-\sum_i \lambda_i A_i}$
GIBBS DISTRIBUTION
$1 = \mathrm{Tr}\,\rho = e^{-(1+\lambda_0)}\,\mathrm{Tr}\left(e^{-\lambda_i A_i}\right)$
$e^{-(1+\lambda_0)} = \frac{1}{Z}$
Z
$Z = \mathrm{Tr}\, e^{-\sum_i \lambda_i A_i}$
PARTITION FUNCTION

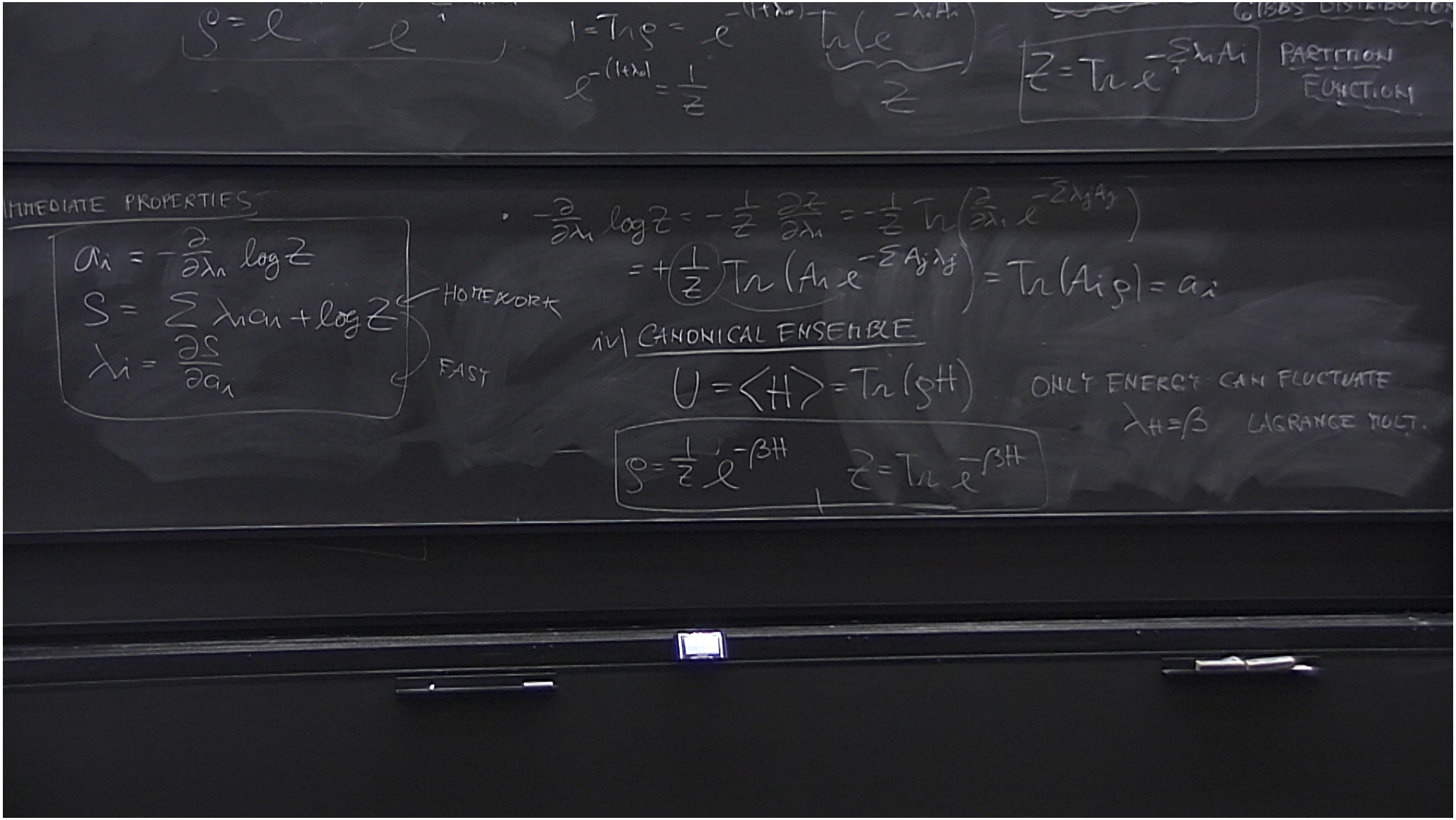
IMMEDIATE PROPERTIES

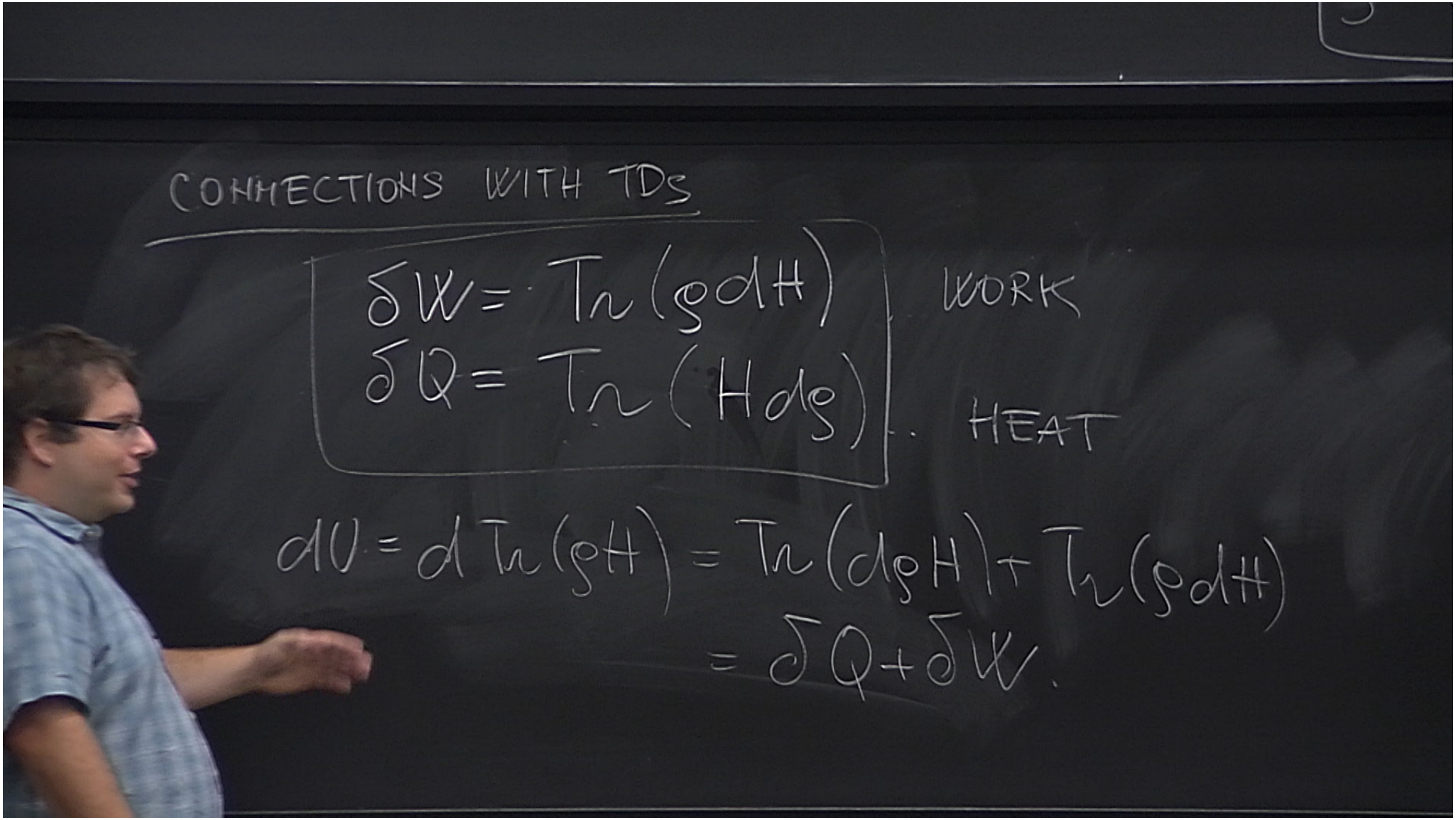
$$a_i = -\frac{\partial}{\partial \lambda_i} \log Z$$

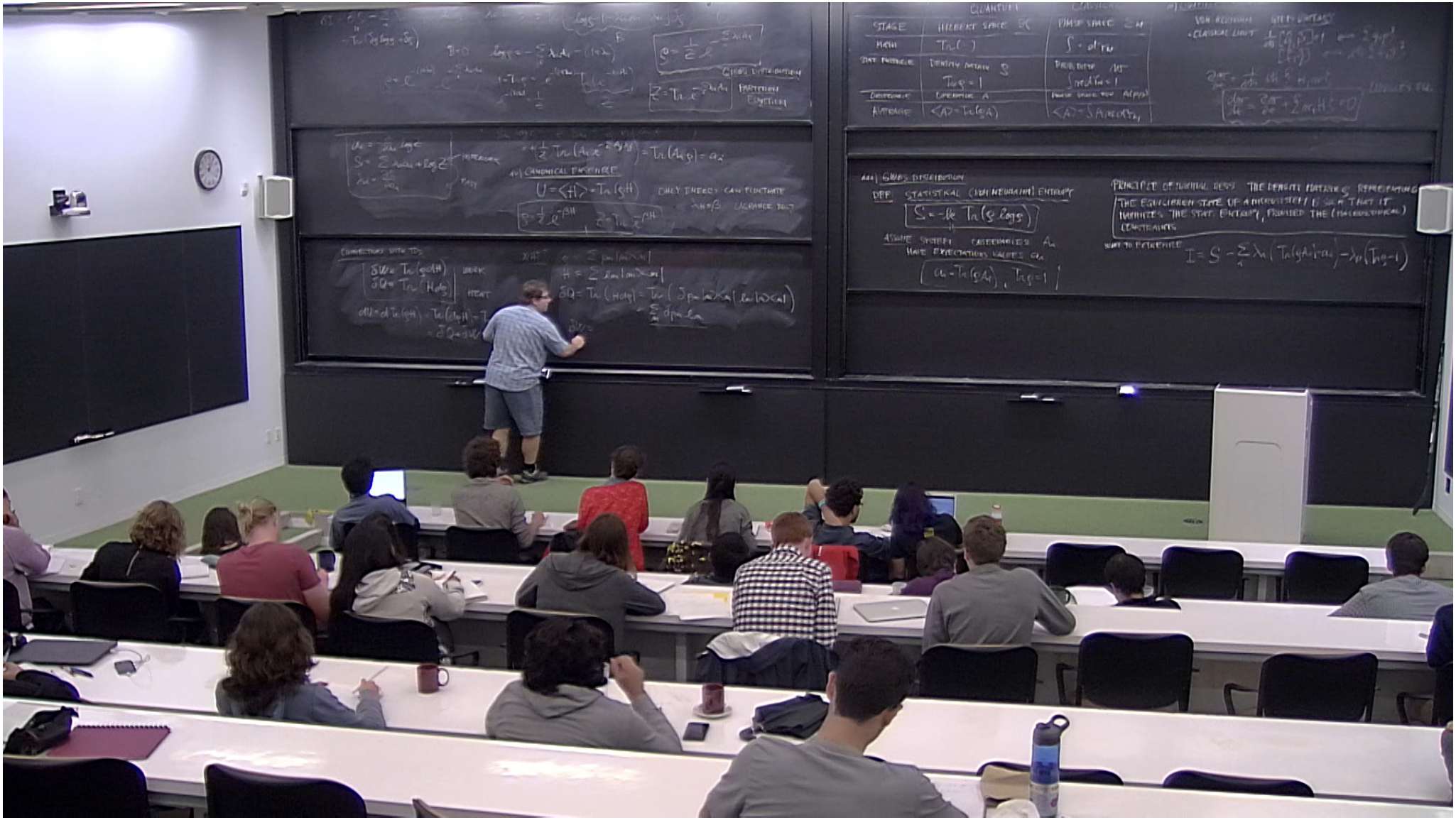
$$S = \sum \lambda_i a_i + \log Z$$

$$\lambda_i = \frac{\partial S}{\partial a_i}$$


B=0
$\log\rho = -\sum_i \lambda_i A_i - (1+\lambda_0)$
$\rho = e^{-(1+\lambda_0)} e^{-\sum_i \lambda_i A_i}$
$1 = \mathrm{Tr}\,\rho = e^{-(1+\lambda_0)} \mathrm{Tr}(e^{-\lambda_i A_i})$
$e^{-(1+\lambda_0)} = \frac{1}{Z}$
Z
$\rho = \frac{1}{Z} e^{-\sum_i \lambda_i A_i}$
$Z = \mathrm{Tr}\, e^{-\sum_i \lambda_i A_i}$
GIBBS
IMMEDIATE PROPERTIES
$a_i = -\frac{\partial}{\partial \lambda_i} \log Z$
$S = \sum \lambda_i a_i + \log Z$
$\lambda_i = \frac{\partial S}{\partial a_i}$
HOMEWORK
FAST
$-\frac{\partial}{\partial \lambda_i} \log Z = -\frac{1}{Z} \frac{\partial Z}{\partial \lambda_i} = -\frac{1}{Z} \mathrm{Tr}\left(\frac{\partial}{\partial \lambda_i} e^{-\sum \lambda_j A_j}\right)$
$= +\frac{1}{Z} \mathrm{Tr}\left(A_i e^{-\sum A_j \lambda_j}\right) = \mathrm{Tr}(A_i \rho) = a_i$


$\rho = e^{-(1+\lambda_0)} e^{-\lambda_i A_i}$
$1 = \mathrm{Tr}\,\rho = e^{-(1+\lambda_0)} \mathrm{Tr}\, e^{-\lambda_i A_i}$
$e^{-(1+\lambda_0)} = \frac{1}{Z}$
Z
GIBBS DISTRIBUTION
$Z = \mathrm{Tr}\, e^{-\sum_i \lambda_i A_i}$
PARTITION FUNCTION
IMMEDIATE PROPERTIES
$a_i = -\frac{\partial}{\partial \lambda_i} \log Z$
$S = \sum \lambda_i a_i + \log Z$
$\lambda_i = \frac{\partial S}{\partial a_i}$
HOMEWORK
FAST
$-\frac{\partial}{\partial \lambda_i} \log Z = -\frac{1}{Z} \frac{\partial Z}{\partial \lambda_i} = -\frac{1}{Z} \mathrm{Tr}\left(\frac{\partial}{\partial \lambda_i} e^{-\sum \lambda_j A_j} \right)$
$= +\frac{1}{Z} \mathrm{Tr}\left(A_i e^{-\sum A_j \lambda_j} \right) = \mathrm{Tr}(A_i \rho) = a_i$
iv) CANONICAL ENSEMBLE
$U = \langle H \rangle = \mathrm{Tr}(\rho H)$
ONLY ENERGY CAN FLUCTUATE
$\lambda_H = \beta$ LAGRANGE MULT.
$\rho = \frac{1}{Z} e^{-\beta H}$
$Z = \mathrm{Tr}\, e^{-\beta H}$


CONNECTIONS WITH TDs
$\delta W = \mathrm{Tr}(\rho\, dH)$ WORK
$\delta Q = \mathrm{Tr}(H\, d\rho)$ HEAT
$dU = d\,\mathrm{Tr}(\rho H) = \mathrm{Tr}(d\rho\, H) + \mathrm{Tr}(\rho\, dH)$
$= \delta Q + \delta W$


STAGE
HILBERT SPACE
PHASE SPACE
GIBBS DISTRIBUTION
PARTITION FUNCTION
CANONICAL ENSEMBLE
DEF. STATISTICAL (VON NEUMANN) ENTROPY
PRINCIPLE OF MAXIMAL IGNORANCE

$\rho = \frac{1}{Z} e^{-\beta H}$, $Z = \mathrm{Tr}\, e^{-\beta H}$

$\hat{H} \equiv \beta$ LAGRANGE MULT.

WHY?

$\rho = \sum p_m |m\rangle\langle m|$

$H = \sum \ell_m |m\rangle\langle m|$

$\delta Q = \mathrm{Tr}(H d\rho) = \mathrm{Tr}\left(\delta p_m |m\rangle\langle m| \ell_n |n\rangle\langle n|\right)$

$= \sum_m \delta p_m \ell_m$

$\delta W = \sum_m p_m \delta \ell_m$

(ρdH)

$\rho = \frac{1}{Z} e^{-\beta H}$ $\quad Z = \mathrm{Tr}\, e^{-\beta H}$

$\hat{H} \equiv \beta$ LAGRANGE MULT.

WHY?

$\rho = \sum p_m |m\rangle\langle m|$

$H = \sum \ell_m |m\rangle\langle m|$

$\delta Q = \mathrm{Tr}(H d\rho) = \mathrm{Tr}\left(\delta p_m |m\rangle\langle m| \ell_m |n\rangle\langle n|\right)$

$= \sum_m \delta p_m \ell_m$

$\delta W = \sum_m p_m \delta \ell_m$ SHIFT ENERGY LEVELS

(ρdH)

GIBBS DISTRIBUTION

PRINCI

DEF: STATISTICAL (VON NEUMANN) ENTROPY

2ND-LAW:

$$\delta S = -\delta \operatorname{Tr}(\rho \log \rho) = -\operatorname{Tr}(\delta\rho \log\rho) - \operatorname{Tr}(\delta\rho)$$

$$= -\operatorname{Tr}\left[\delta\rho\left(-\beta H - \log Z\right)\right]$$

$$= +\operatorname{Tr}(\delta\rho\,\beta H) = \beta \operatorname{Tr}(\delta\rho H) = \beta\,\delta Q$$

DEF: STATISTICAL ENTROPY

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

THE EQ
MAXIMIZE

2ND-LAW:

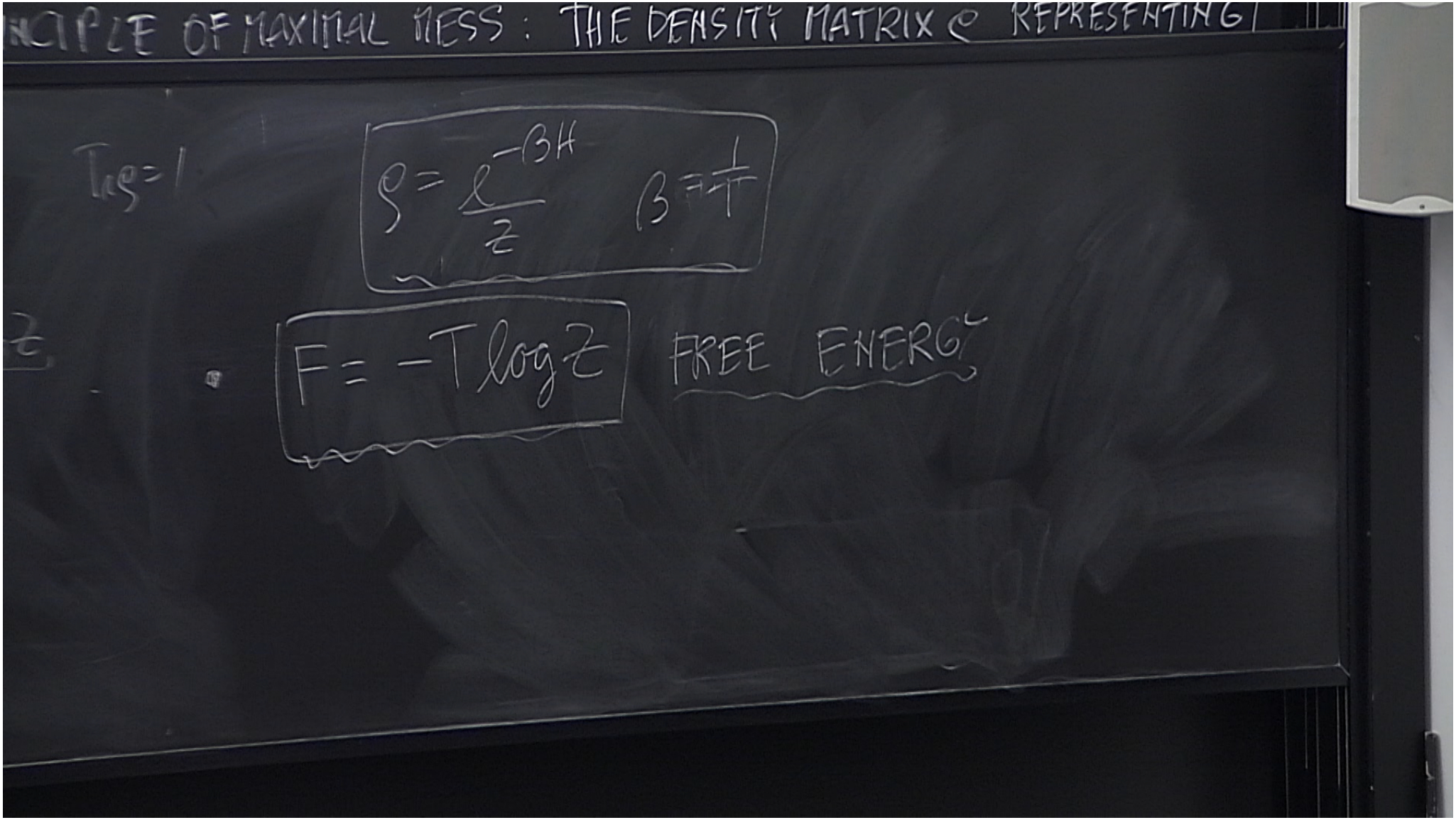
$$\delta S = -\delta \, \mathrm{Tr}(\rho \log \rho) = -\mathrm{Tr}(\delta\rho \log \rho) - \mathrm{Tr}(\delta\rho)$$

$$= -\mathrm{Tr}\left[\delta\rho\,(-\beta H - \log Z)\right] = +\mathrm{Tr}\,\delta\rho(\beta H) + \mathrm{Tr}(\delta\rho)\log Z$$

$$= +\mathrm{Tr}(\delta\rho\,\beta H) = \beta\,\mathrm{Tr}(\delta\rho H) = \beta\,\delta Q$$

REMIND CLAUSIUS: $\delta S = \dfrac{\delta Q}{T}$

$$\beta = \frac{1}{T}$$


NCIPLE OF MAXIMAL MESS: THE DENSITY MATRIX & REPRESENTING
Tr ρ = 1
ρ = e^{-βH} / Z
β = 1/T
Z
F = -T log Z
FREE ENERGY

CONNECTIONS WITH TDs

IMMEDIATE PROPERTIES

$$a_i = -\frac{\partial}{\partial \lambda_i} \log Z$$

$$S = \sum \lambda_i a_i + \log Z$$

$$\lambda_i = \frac{\partial S}{\partial a_i}$$

HOMEWORK

FAST

$$S = \beta U + \log Z$$

$$TS = U + T \log Z$$

WHY?

$$\cdot\ -\frac{\partial}{\partial \lambda_i} \log Z = -\frac{1}{Z} \frac{\partial Z}{\partial \lambda_i} = -\frac{1}{Z} \mathrm{Tr}\left(\frac{\partial}{\partial \lambda_i} e^{-\sum \lambda_j A_j} \right)$$

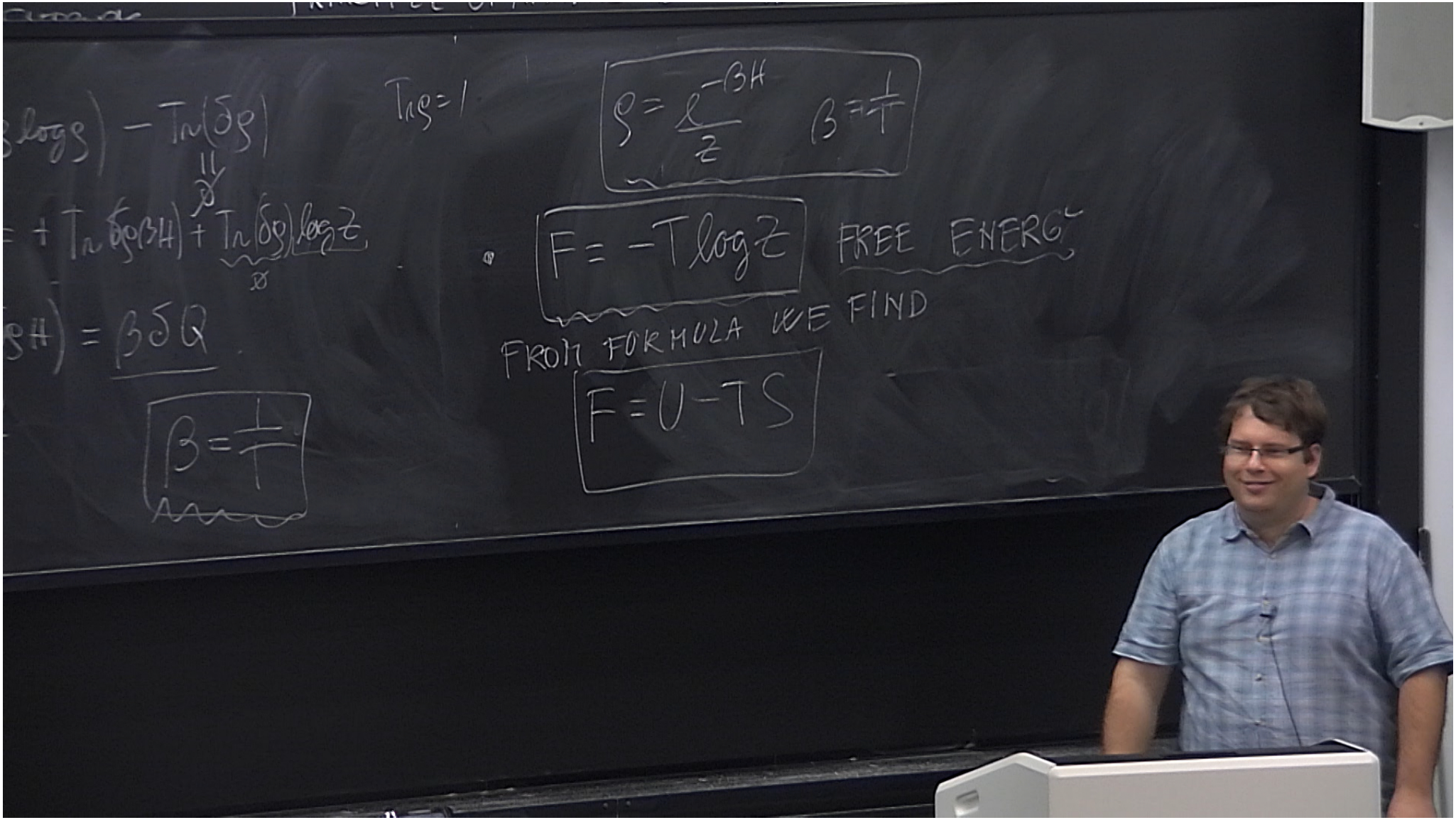
$$= +\frac{1}{Z} \mathrm{Tr}\left(A_i e^{-\sum A_j \lambda_j} \right) = \mathrm{Tr}(A_i \rho)$$

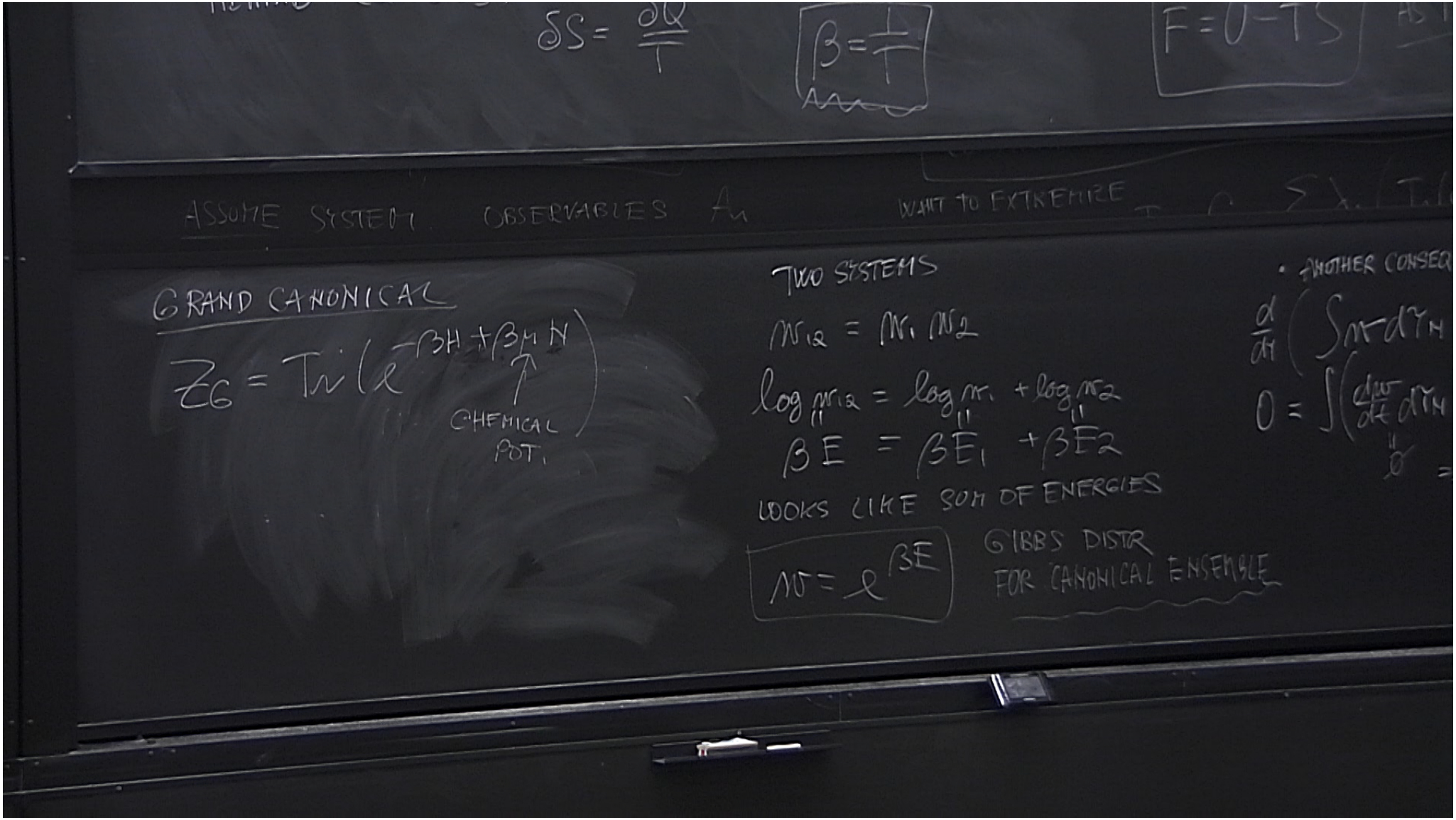
iv) CANONICAL ENSEMBLE

$$U = \langle H \rangle = \mathrm{Tr}(\rho H)$$

ONLY EN

$$\rho = \frac{1}{Z} e^{-\beta H} \qquad Z = \mathrm{Tr}\, e^{-\beta H}$$


$\rho = \frac{e^{-\beta H}}{Z}$ $\beta = \frac{1}{T}$
$F = -T \log Z$ FREE ENERGY
FROM FORMULA WE FIND
$F = U - TS$
$\beta = \frac{1}{T}$


$\delta S = \frac{\delta Q}{T}$
$\beta = \frac{1}{T}$
$F = U - TS$
ASSUME SYSTEM OBSERVABLES A_n
WANT TO EXTREMIZE
GRAND CANONICAL
$Z_G = Tr\left(e^{-\beta H + \beta\mu N}\right)$
CHEMICAL POT.
TWO SYSTEMS
$\Omega_{12} = \Omega_1 \Omega_2$
$\log \Omega_{12} = \log \Omega_1 + \log \Omega_2$
$\beta E = \beta E_1 + \beta E_2$
LOOKS LIKE SUM OF ENERGIES
$\Omega = e^{\beta E}$
GIBBS DISTR FOR CANONICAL ENSEMBLE
ANOTHER CONSEQ
$\frac{\partial}{\partial \mu}\left(\sum \pi d\gamma_N\right)$
$0 = \int \left(\frac{\partial \ln \Omega}{\partial E} d\gamma_N\right)$