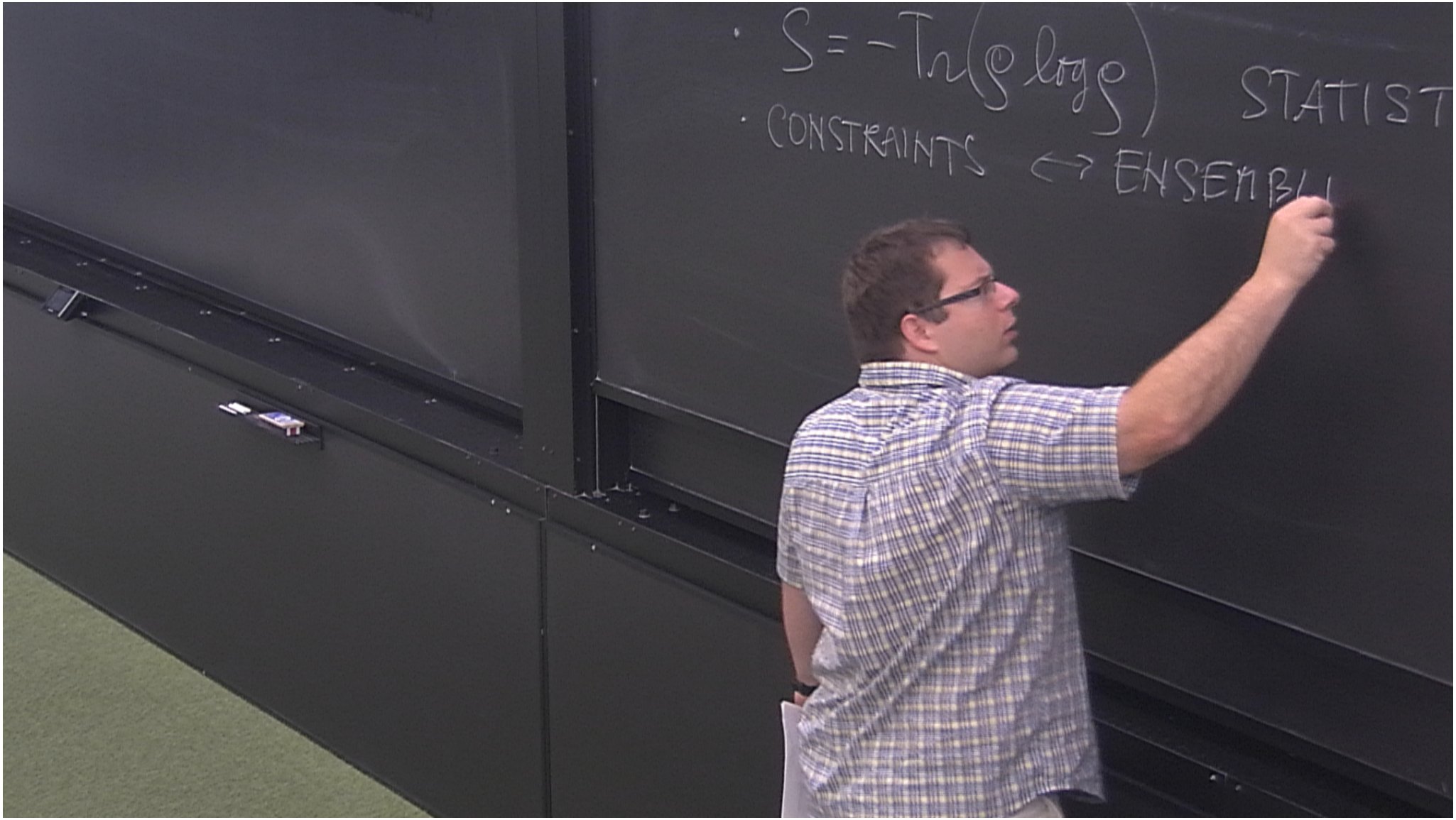
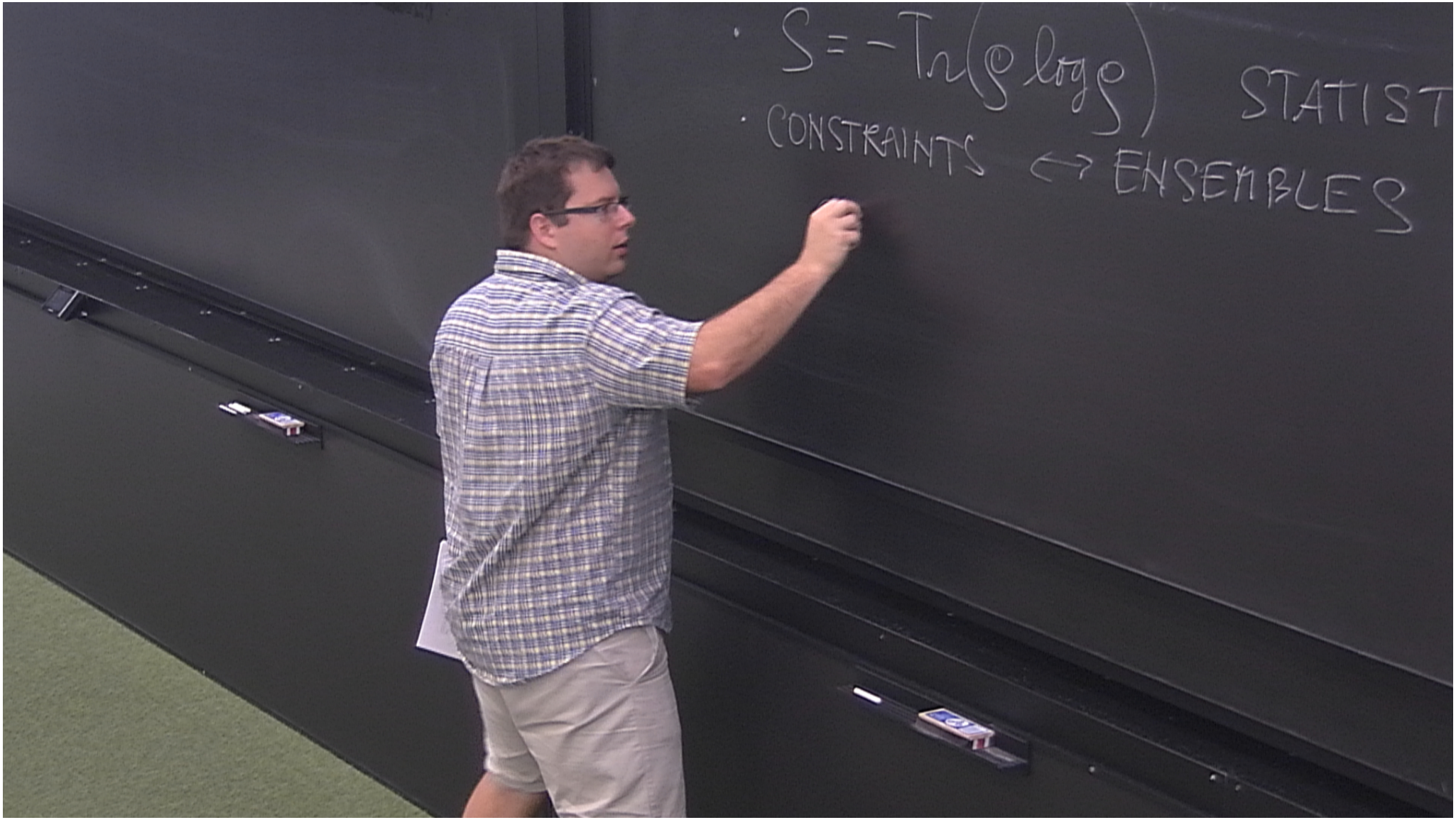
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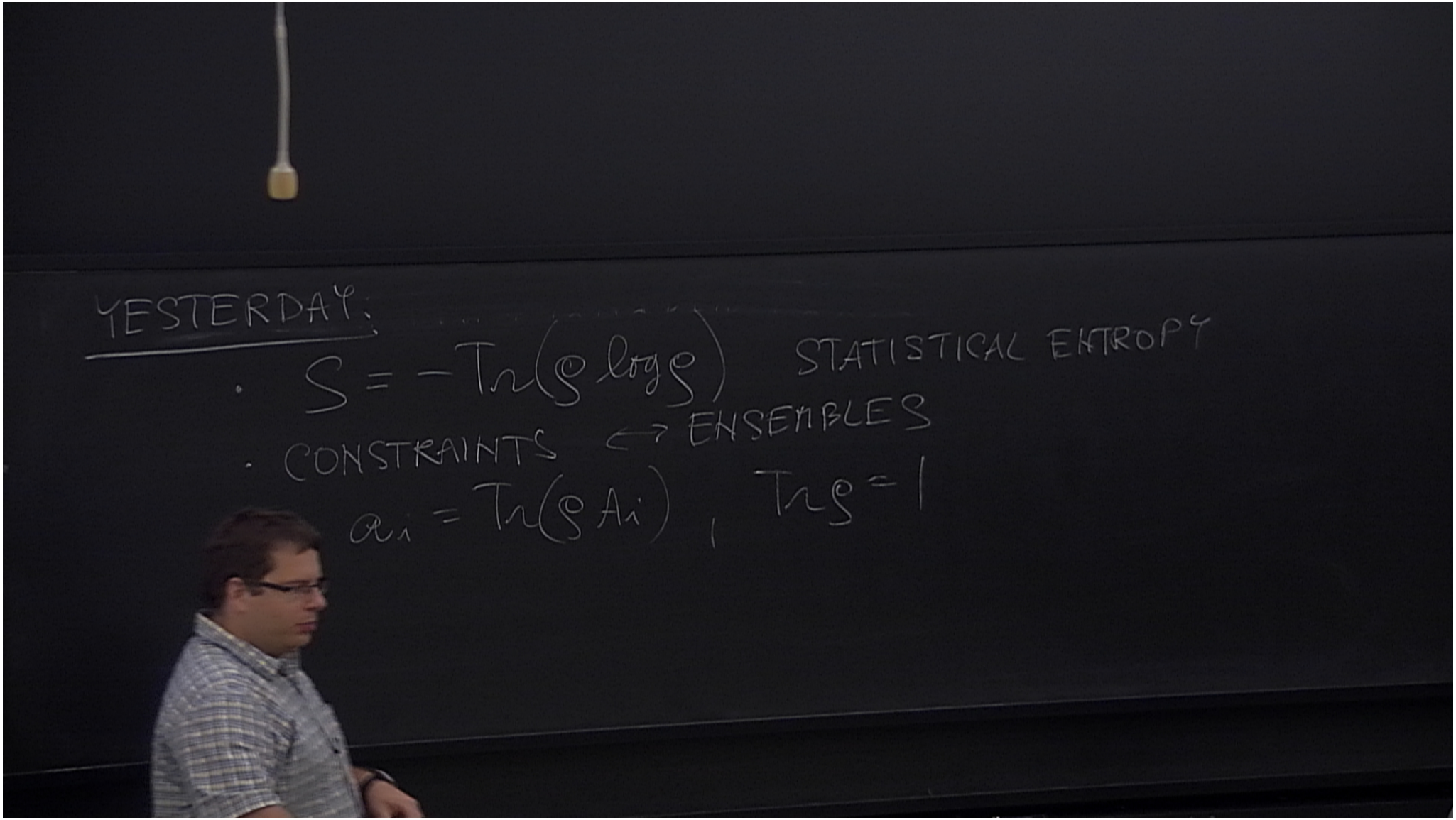
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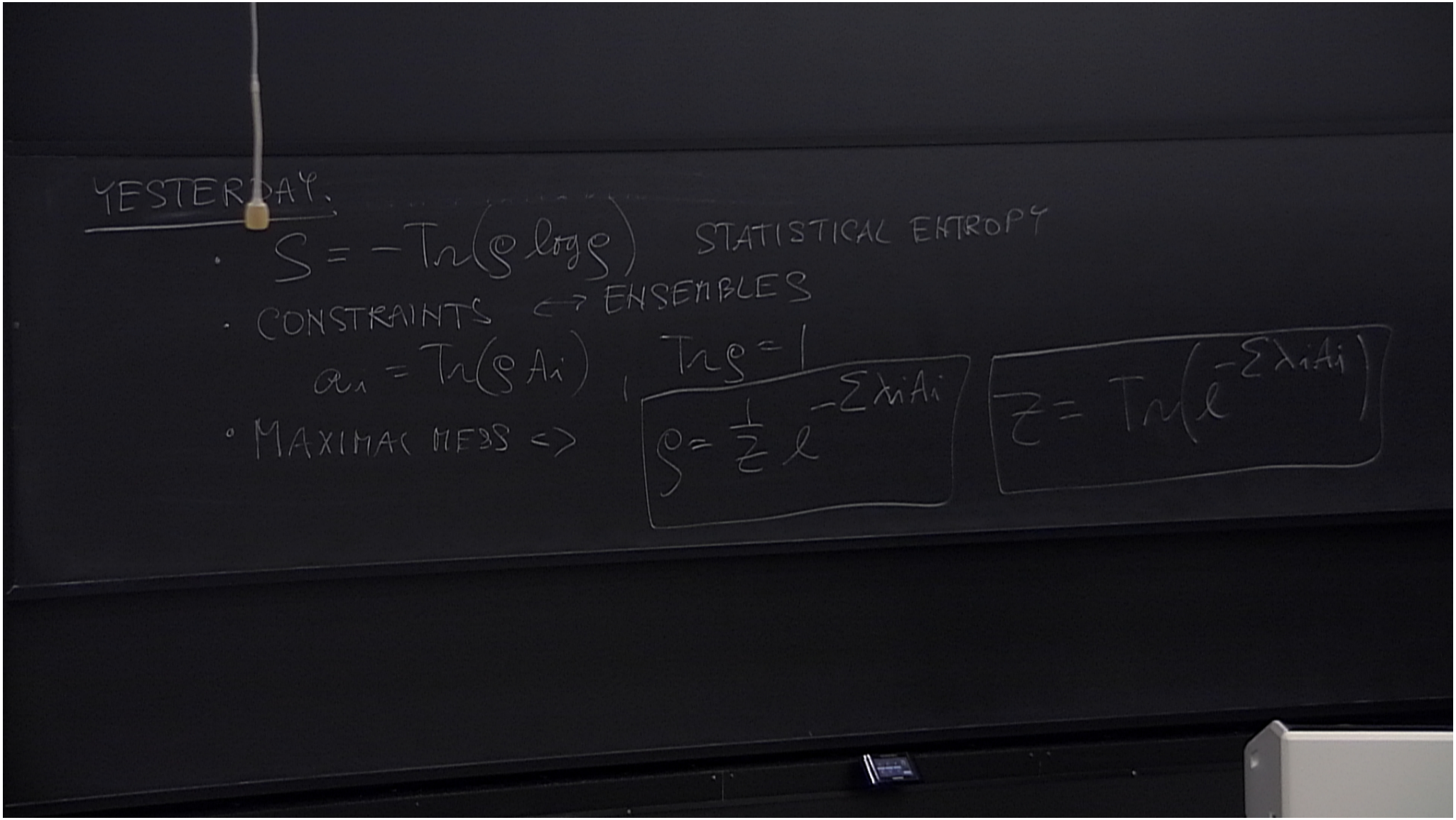
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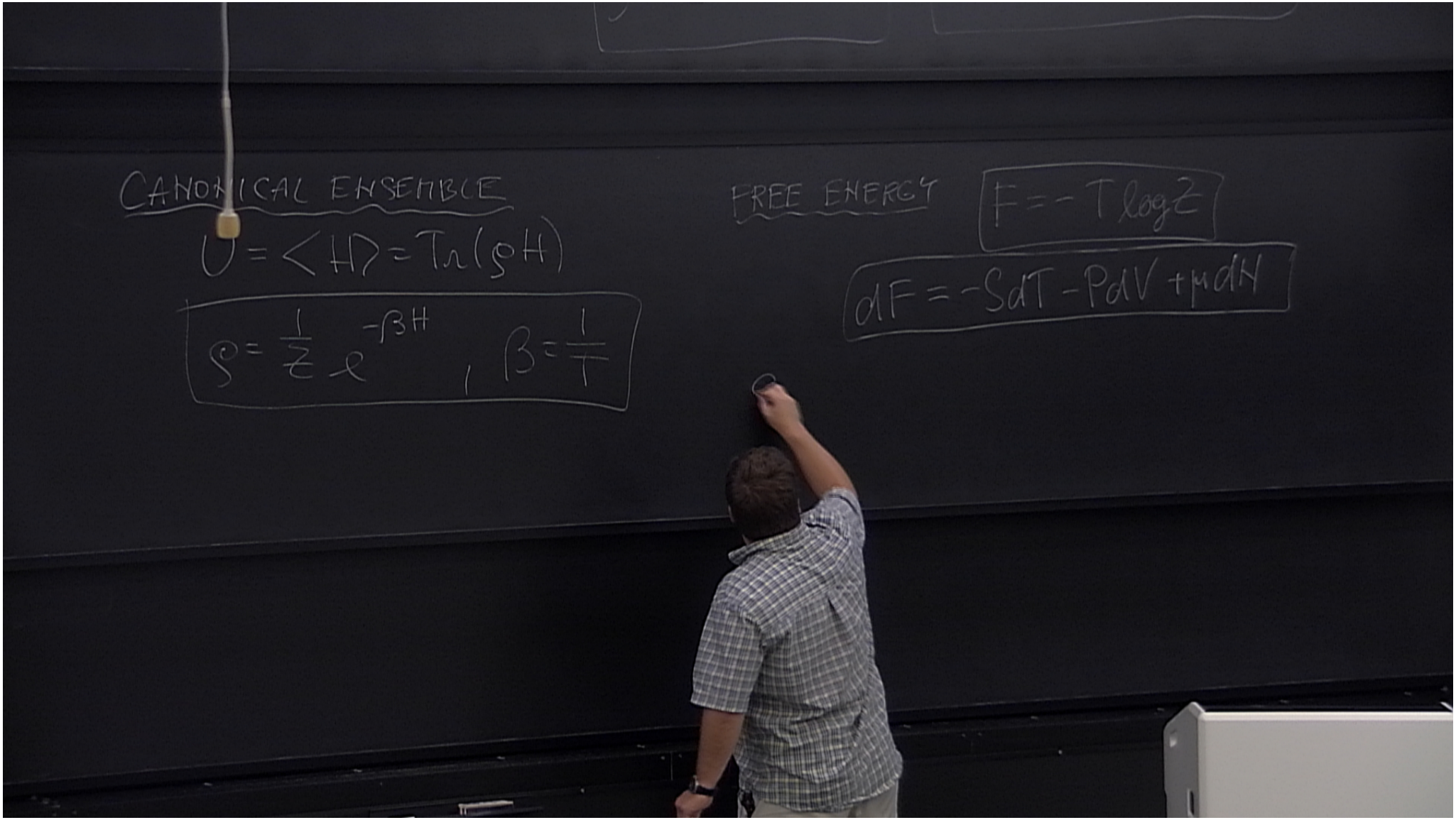
Abstract:

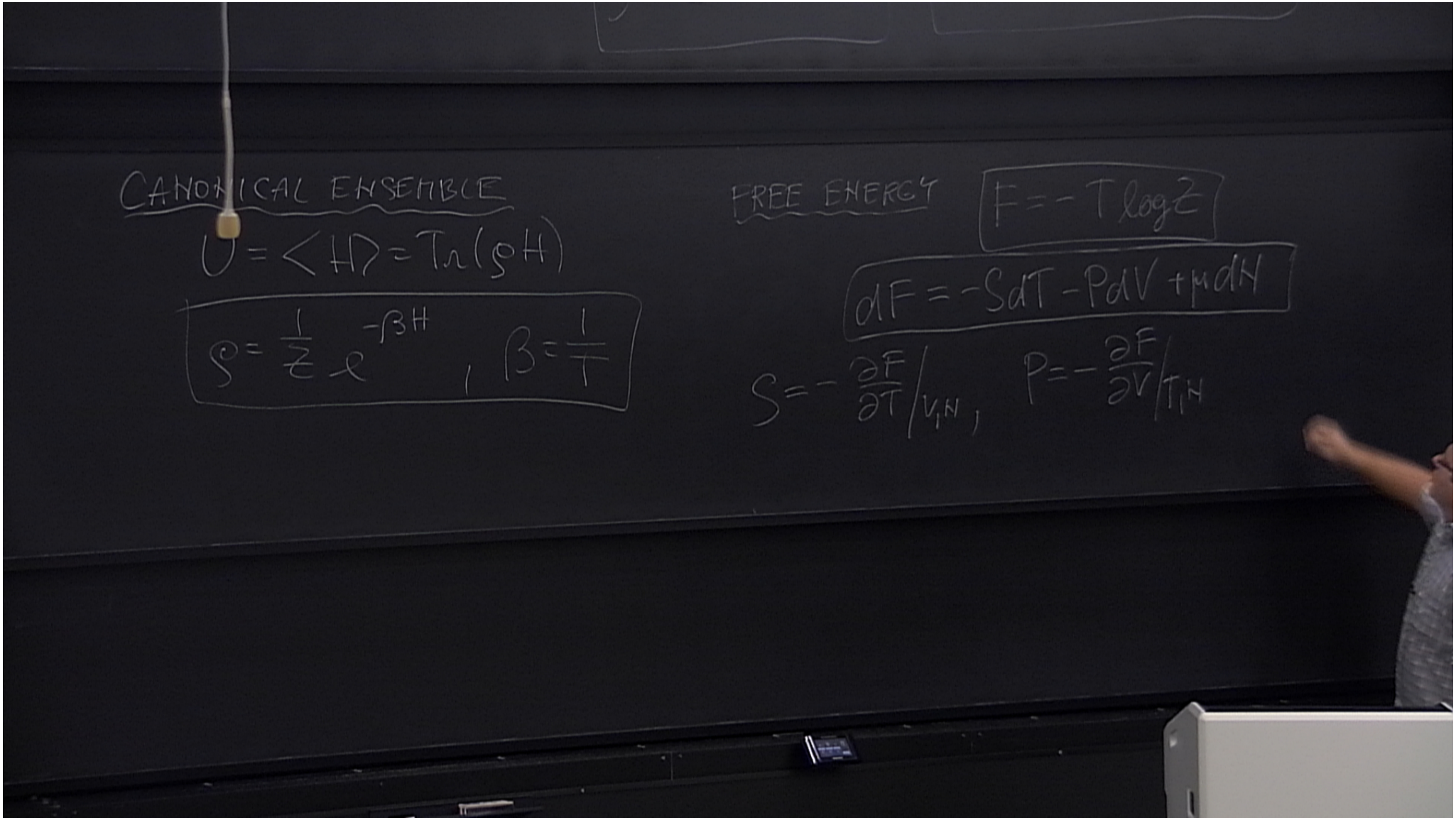

S = -Tr(ρ log ρ)
STATIST
CONSTRAINTS ↔ ENSEMBL

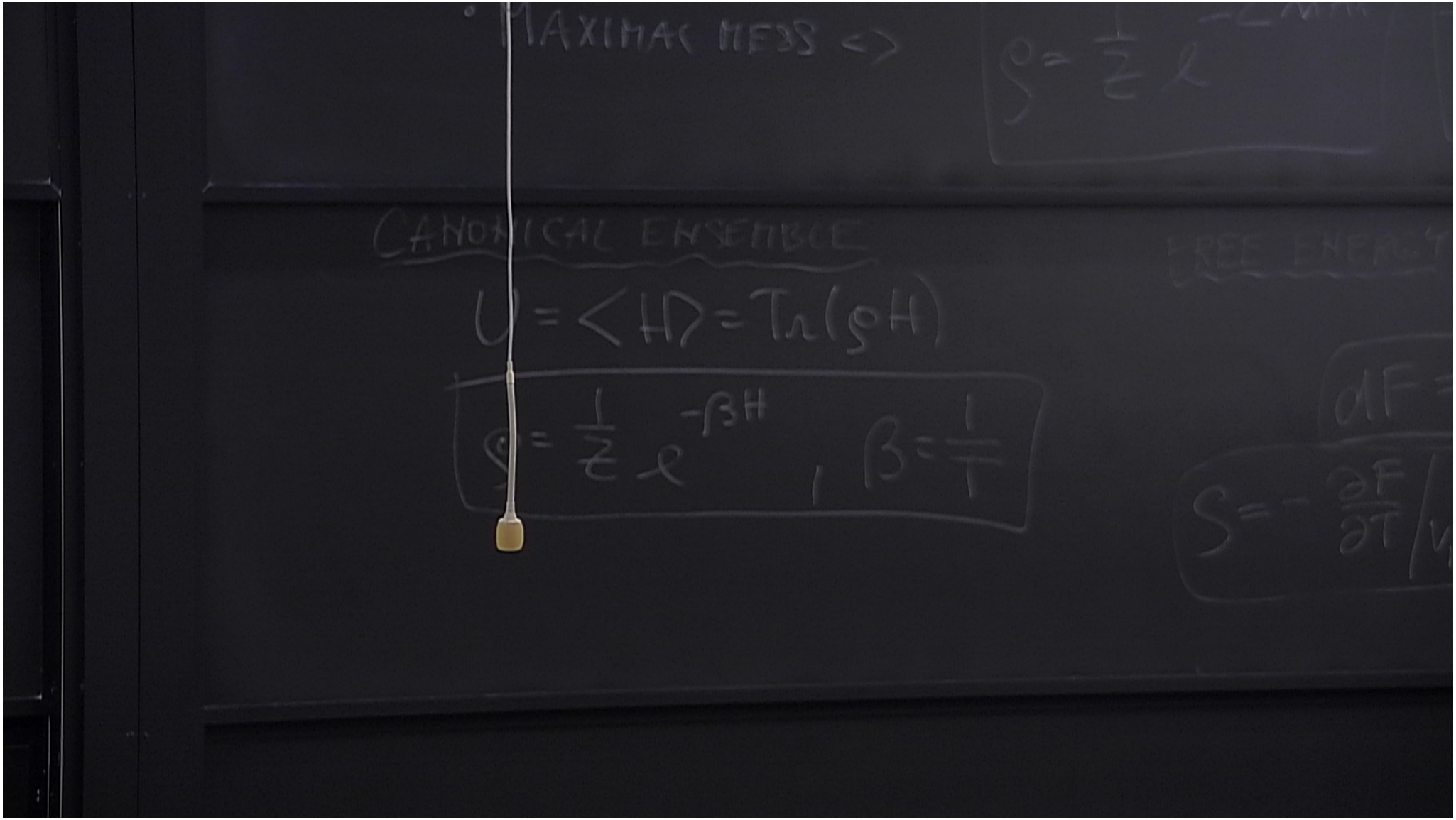

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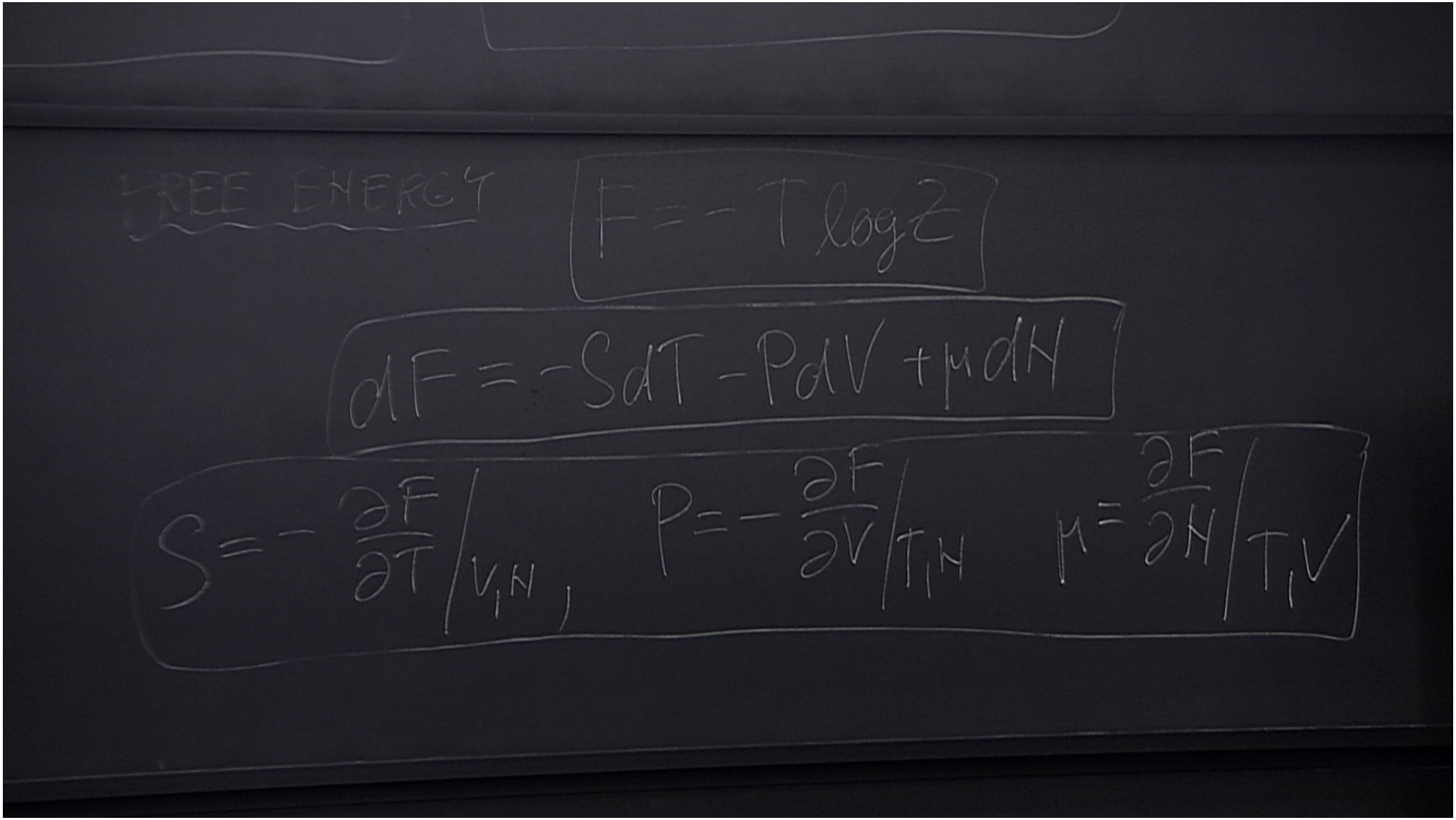

YESTERDAY:
$S = -\mathrm{Tr}(\rho \log \rho)$ STATISTICAL ENTROPY
CONSTRAINTS $\leftrightarrow$ ENSEMBLES
$a_i = \mathrm{Tr}(\rho A_i)$, $\mathrm{Tr}\rho = 1$

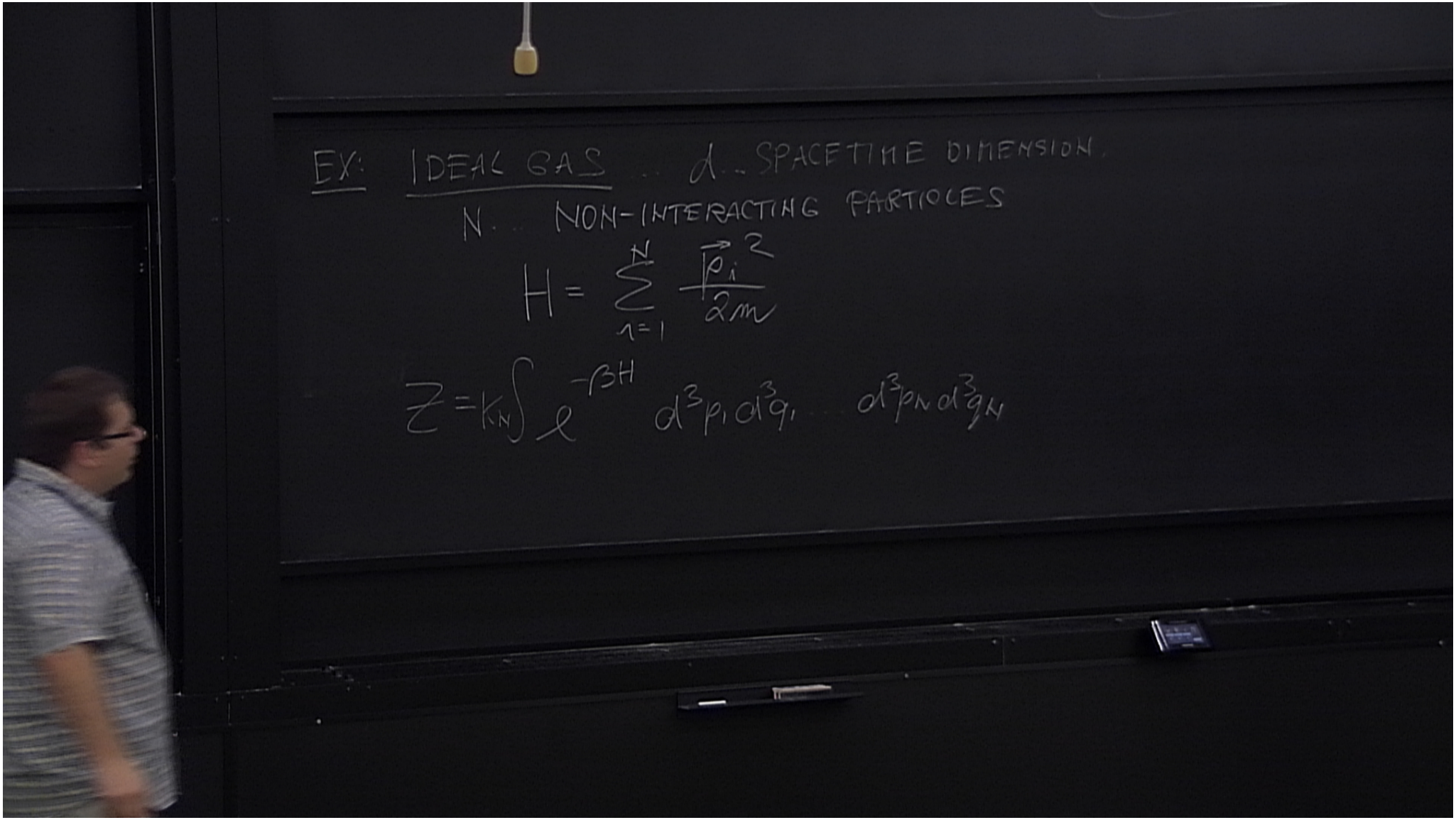

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$S = -\mathrm{Tr}(\rho \log \rho)$ STATISTICAL ENTROPY
CONSTRAINTS ↔ ENSEMBLES
$a_i = \mathrm{Tr}(\rho A_i)$, $\mathrm{Tr}\rho = 1$
MAXIMAL MESS ↔
$\rho = \frac{1}{Z} e^{-\sum \lambda_i A_i}$
$Z = \mathrm{Tr}\left(e^{-\sum \lambda_i A_i}\right)$

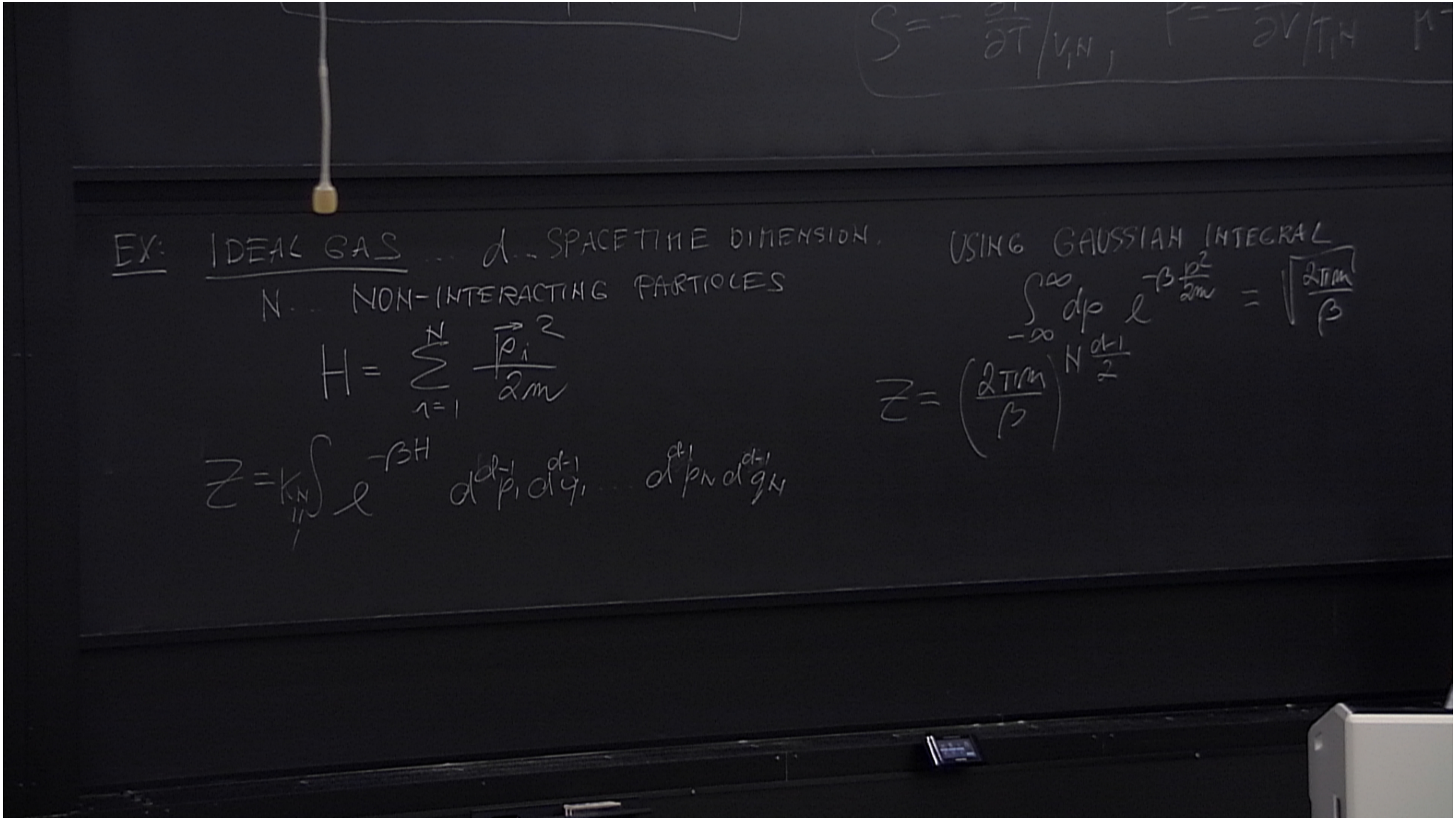

CANONICAL ENSEMBLE
$U = \langle H \rangle = Tr(\rho H)$
$\rho = \frac{1}{Z} e^{-\beta H}$, $\beta = \frac{1}{T}$
FREE ENERGY
$F = -T \log Z$
$dF = -SdT - PdV + \mu dN$

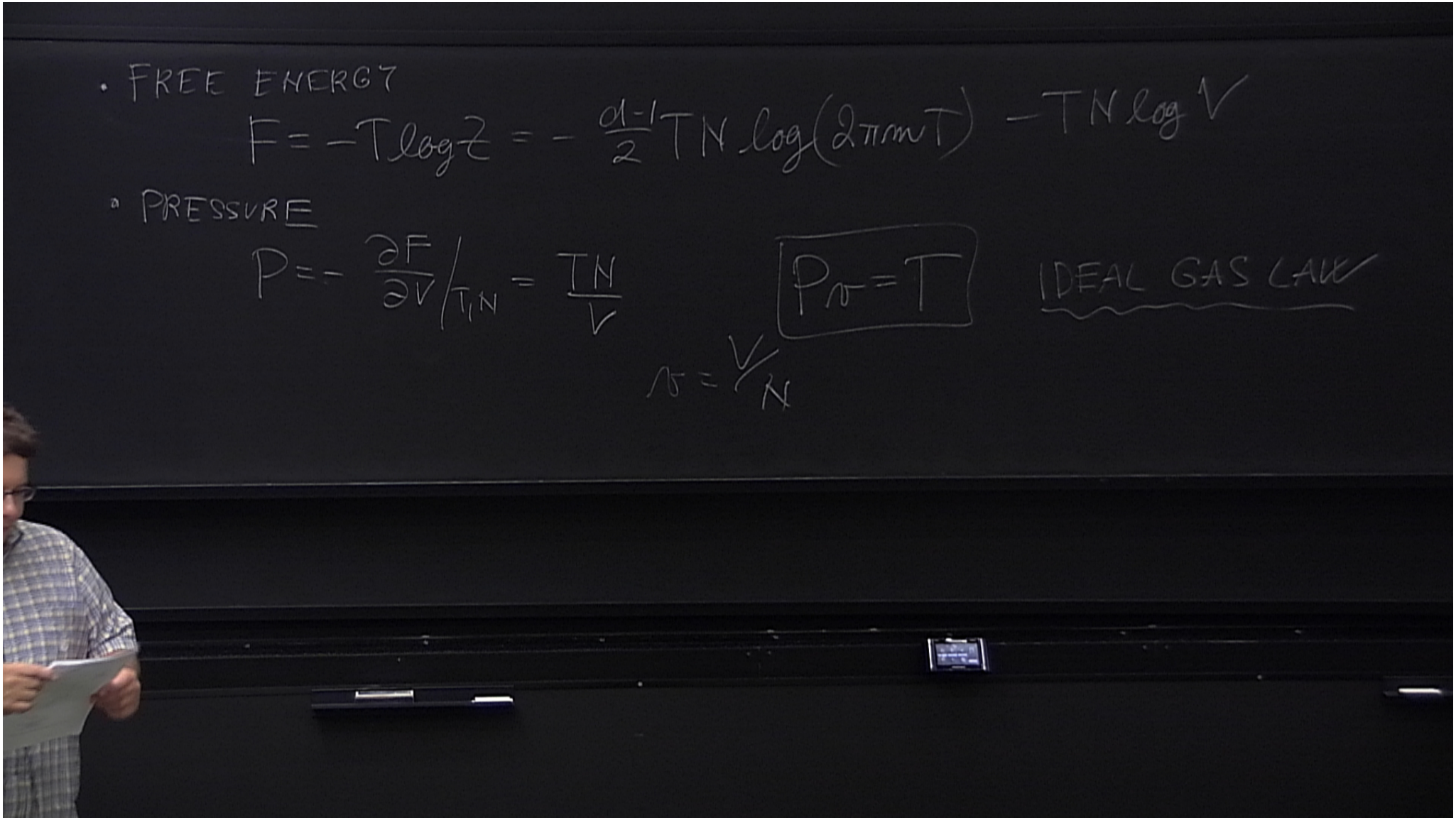

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$S = -\frac{\partial F}{\partial T}\Big|_{V,N}$, $P = -\frac{\partial F}{\partial V}\Big|_{T,N}$

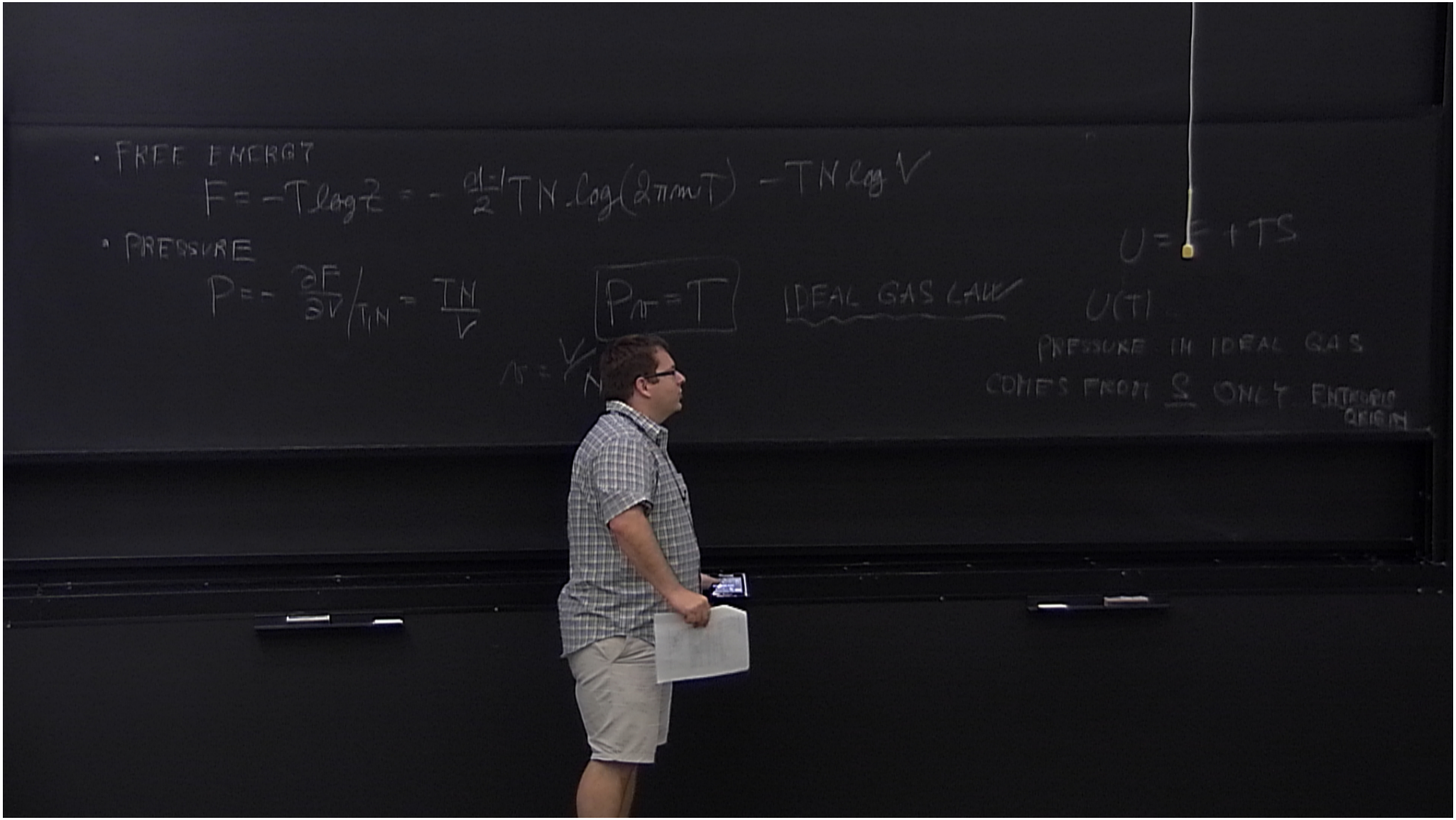

MAXIMAL MESS <>

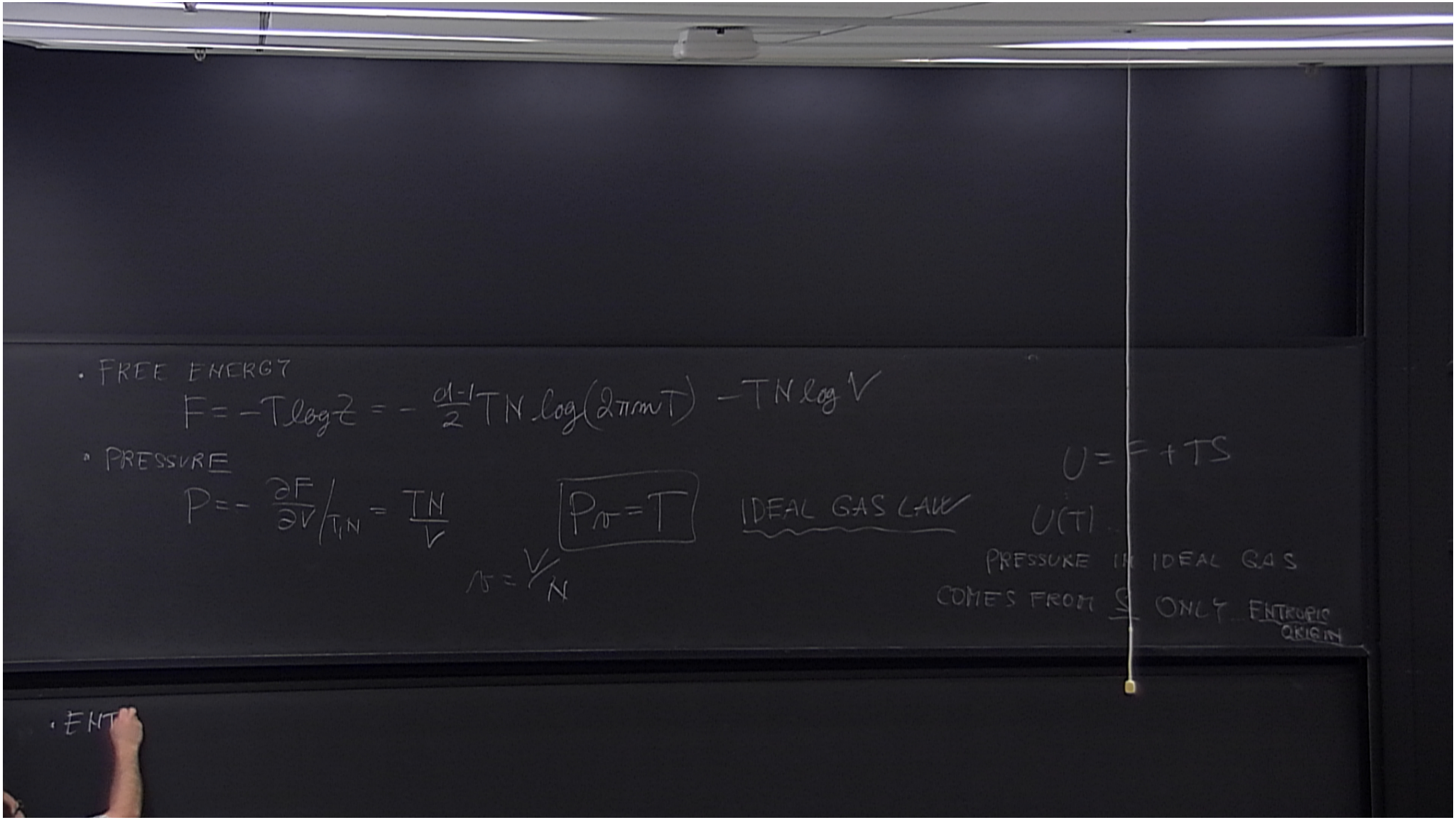

FREE ENERGY
$F = -T \log Z$
$dF = -S dT - P dV + \mu dN$
$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}$, $P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$ $\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}$

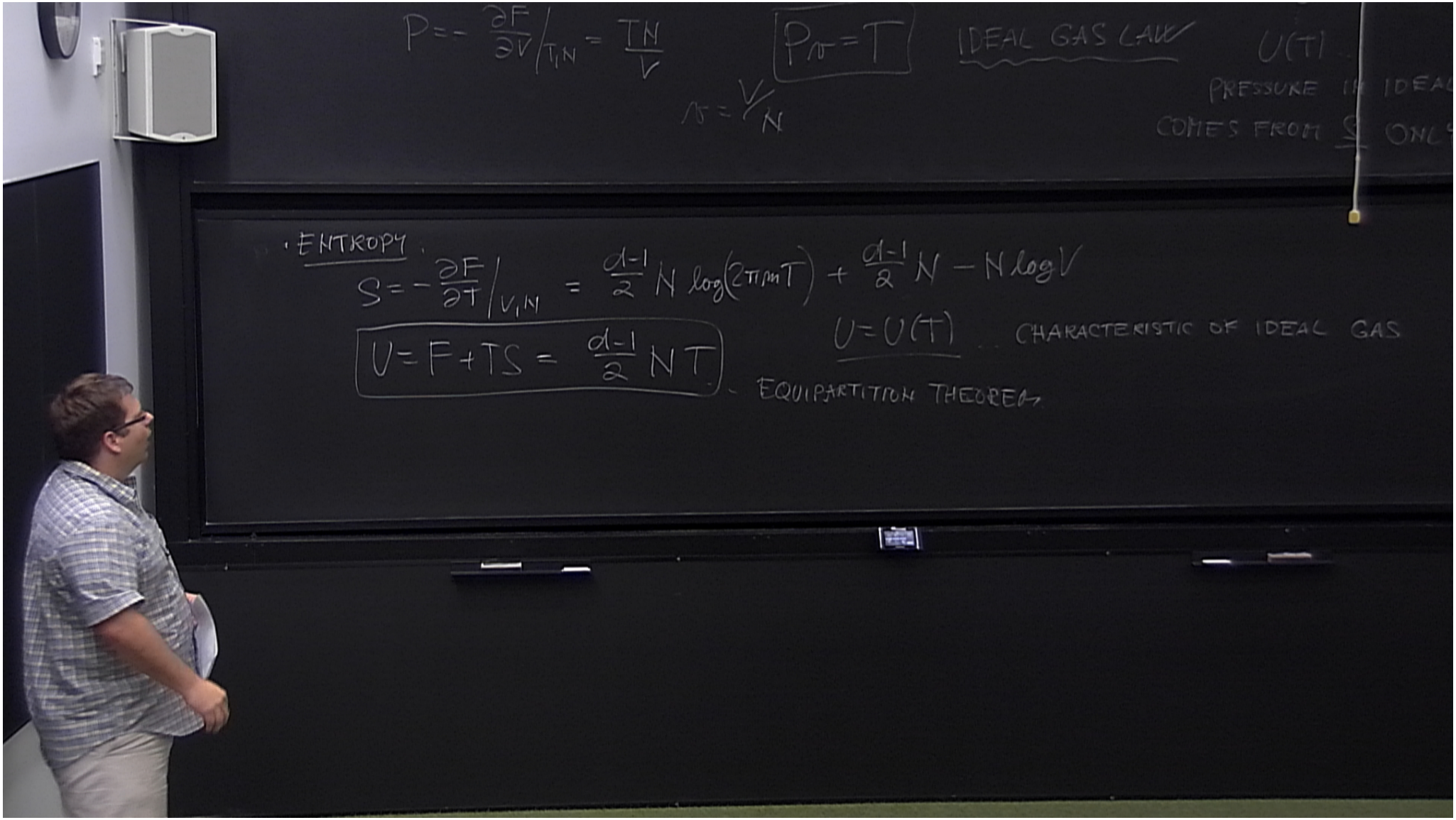

EX: IDEAL GAS ... d ... SPACETIME DIMENSION.
N ... NON-INTERACTING PARTICLES
$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$
$Z = K_N \int e^{-\beta H} d^3p_1 d^3q_1 \cdots d^3p_N d^3q_N$

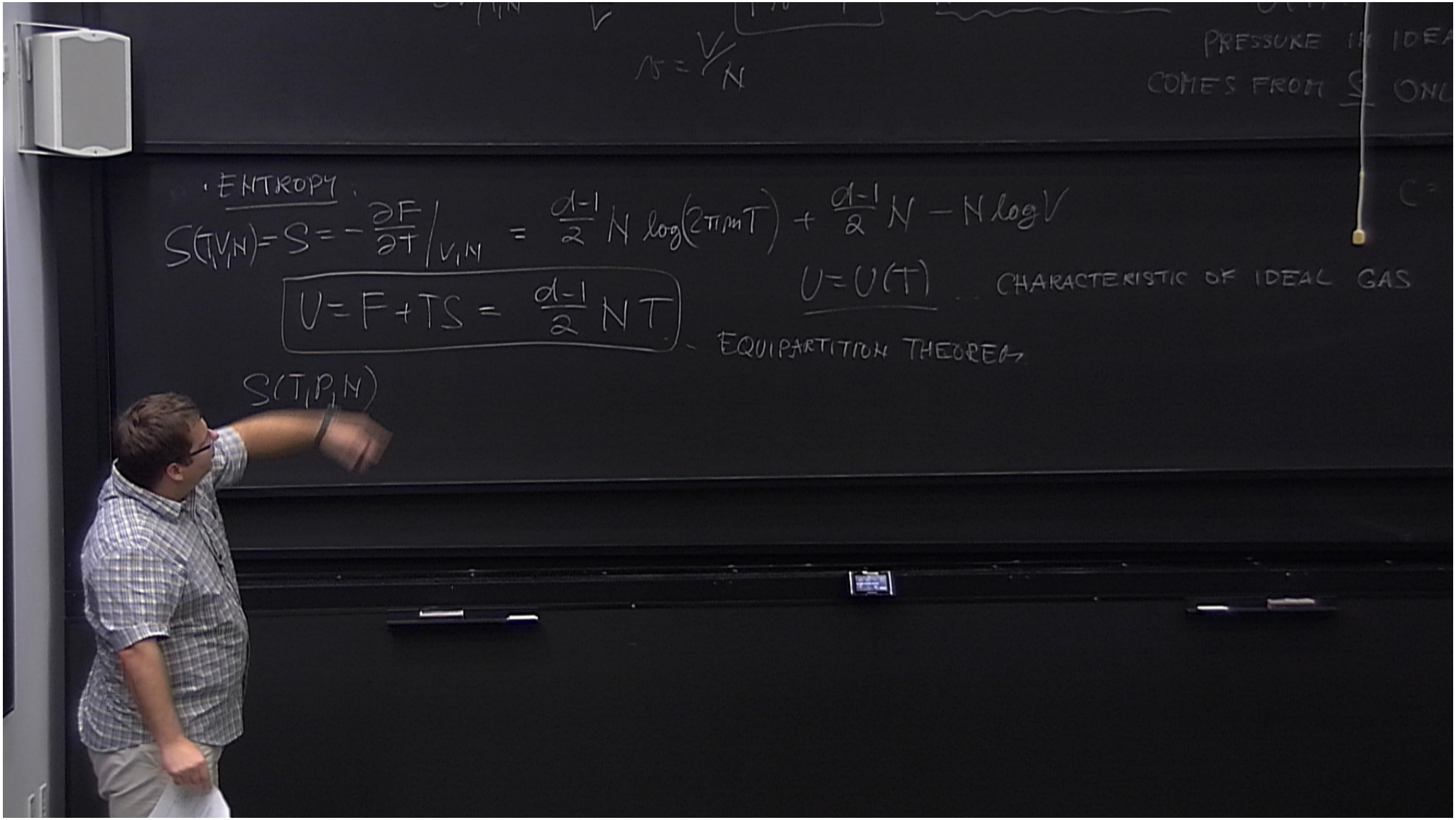

EX: IDEAL GAS ... d ... SPACETIME DIMENSION.
N ... NON-INTERACTING PARTICLES
USING GAUSSIAN INTEGRAL
$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$
$\int_{-\infty}^{\infty} dp\, e^{-\beta \frac{p^2}{2m}} = \sqrt{\frac{2\pi m}{\beta}}$
$Z = \left(\frac{2\pi m}{\beta}\right)^{N \frac{d-1}{2}}$
$Z = K_N \int e^{-\beta H} d^{d-1}p_1 d^{d-1}q_1 \cdots d^{d-1}p_N d^{d-1}q_N$

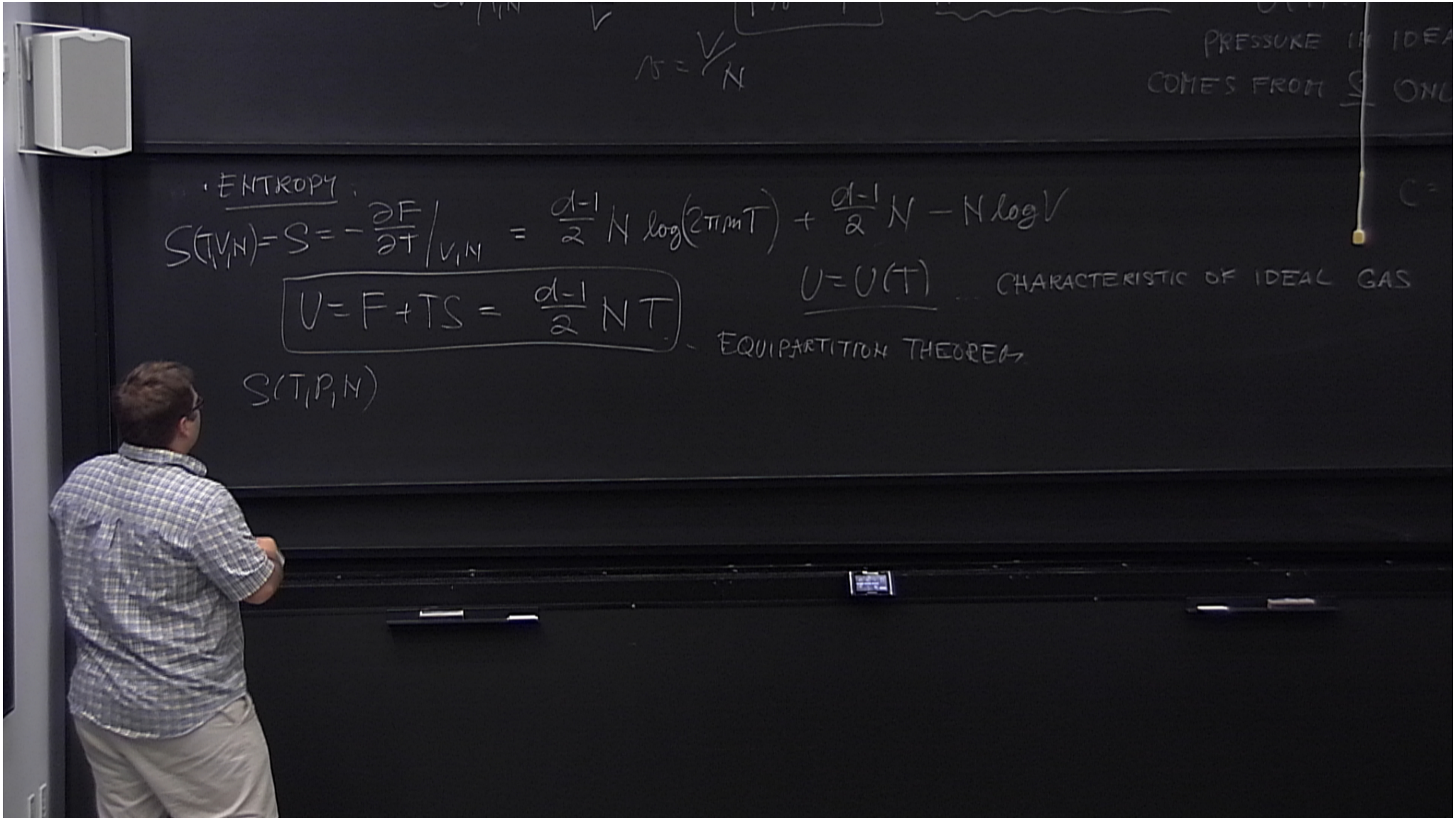

• FREE ENERGY
$F = -T \log Z = -\frac{d-1}{2} T N \log(2\pi m T) - T N \log V$
• PRESSURE
$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{TN}{V}$
$P v = T$
IDEAL GAS LAW
$v = V/N$

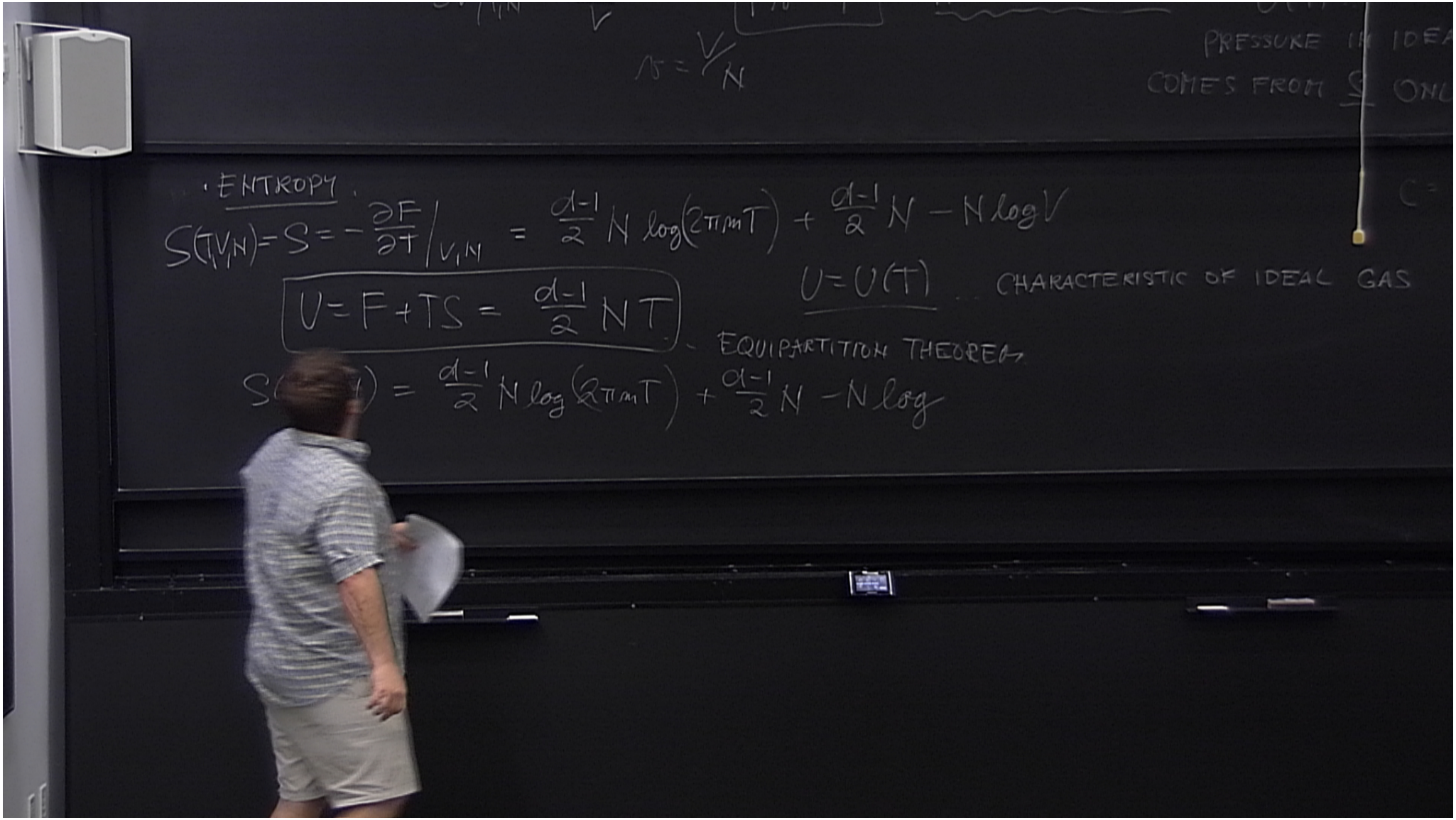

• FREE ENERGY
F = −T log Z = − (3/2) TN log(2πmT) − TN log V
• PRESSURE
P = − (∂F/∂V)|T,N = TN/V
PV = T
IDEAL GAS LAW
U = F + TS
U(T)
PRESSURE IN IDEAL GAS
COMES FROM S ONLY. ENTROPIC
ORIGIN


• FREE ENERGY
$F = -T \log Z = -\frac{d-1}{2} T N \log(2\pi m T) - T N \log V$
• PRESSURE
$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{TN}{V}$
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$U = F + TS$
$U(T)$
PRESSURE IN IDEAL GAS
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• ENT


$P = -\frac{\partial F}{\partial V}\Big|_{T,N} = \frac{TN}{V}$
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IDEAL GAS LAW
$v = V/N$
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PRESSURE IN IDEA
COMES FROM
ONL
ENTROPY
$S = -\frac{\partial F}{\partial T}\Big|_{V,N} = \frac{d-1}{2} N \log(2\pi m T) + \frac{d-1}{2} N - N \log V$
$U = F + TS = \frac{d-1}{2} NT$
$U = U(T)$
CHARACTERISTIC OF IDEAL GAS
EQUIPARTITION THEOREM


$n = V/N$
PRESSURE IN IDEA
COMES FROM
· ENTROPY
$S(T,V,N) = S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = \frac{d-1}{2} N \log(2\pi m T) + \frac{d-1}{2} N - N \log V$
$U = F + TS = \frac{d-1}{2} NT$
$U = U(T)$
CHARACTERISTIC OF IDEAL GAS
EQUIPARTITION THEOREM
$S(T,P,N)$


PRESSURE IN IDEA
COMES FROM
ONC
ENTROPY
$S(T,V,N) = S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = \frac{d-1}{2} N \log(2\pi m T) + \frac{d-1}{2} N - N \log V$
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EQUIPARTITION THEOREM
$S(T,P,N)$


PRESSURE IN IDEA
COMES FROM
ONL
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$U = F + TS = \frac{d-1}{2} NT$
$U = U(T)$
CHARACTERISTIC OF IDEAL GAS
EQUIPARTITION THEOREM
$= \frac{d-1}{2} N \log(2\pi m T) + \frac{d-1}{2} N - N \log$

$$S(T,P,N) = \frac{d-1}{2} N \log\left(2\pi m T\right) + \frac{d-1}{2} N - N \log\left(\frac{TN}{P}\right)$$

- SPECIFIC HEAT

$$C_{\alpha,\beta,\ldots} = \frac{\delta Q_{\alpha,\beta,\ldots}}{dT}$$

$$C_V = \frac{\delta Q}{dT}\Big|_{V,N} = T \frac{\partial S}{\partial T}\Big|_{V,N} = \frac{d-1}{2} N$$

$$C_P = T \frac{\partial S}{\partial T}\Big|_{P,N}$$



$\frac{1}{2}NT$

EQUIPARTITION THEOREM

$$N\log\left(2\pi m T\right) + \frac{d-1}{2}N - N\log\left(\frac{N}{P}\right)$$

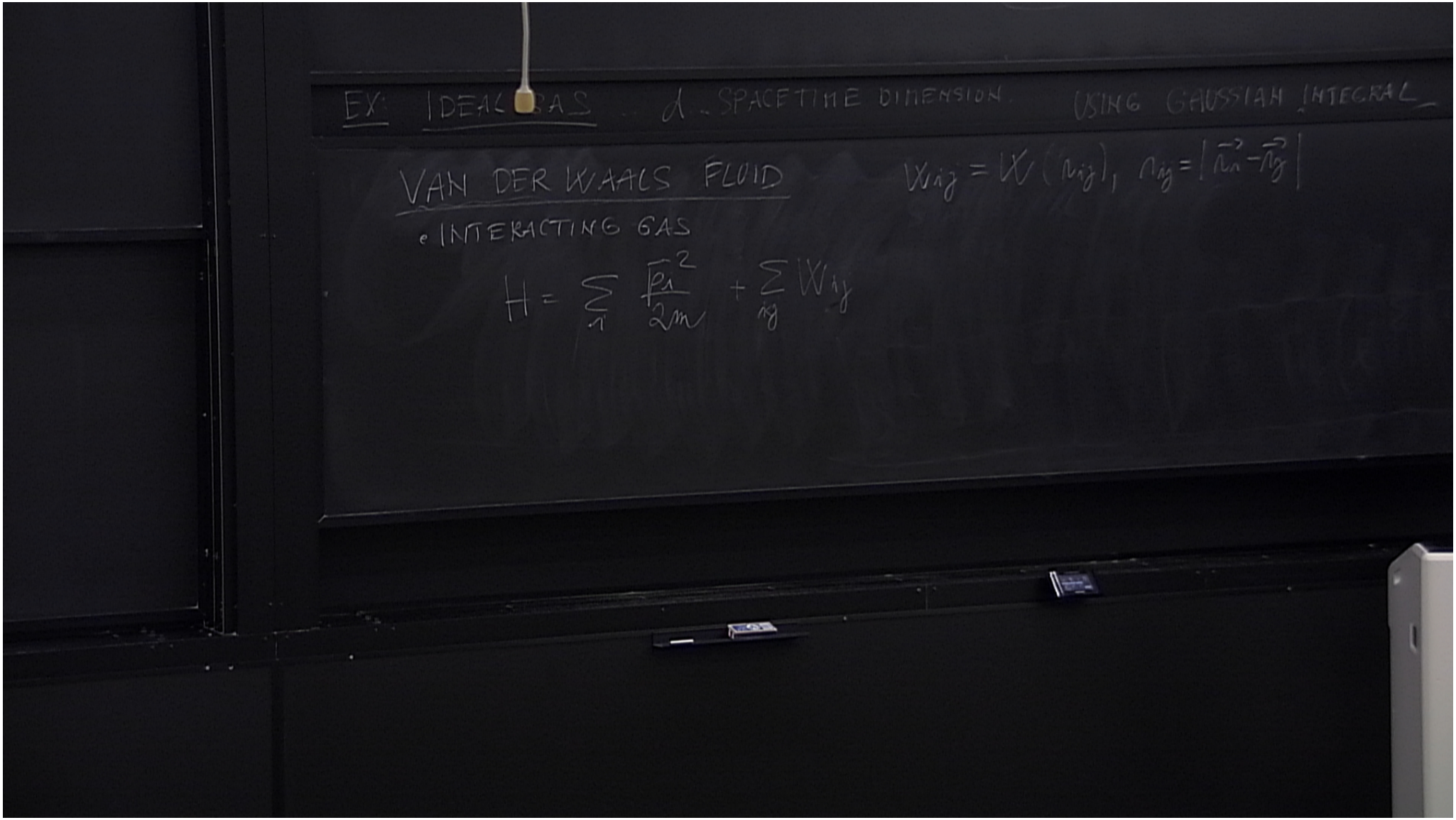
$$C_{\alpha\beta} = \frac{\partial Q_{\alpha\beta}}{dT}$$

$$\frac{Q}{T}\Big|_{V,N} = T\frac{\partial S}{\partial T}\Big|_{V,N} = \frac{d-1}{2}N$$

$$\frac{\partial S}{\partial T}\Big|_{P,N} = \frac{d+1}{2}N$$

MYER'S LAW

$$\gamma = \frac{C_P}{C_V} = \frac{d+1}{d-1} \approx \frac{5}{3}$$


EX: IDEAL GAS d - SPACETIME DIMENSION USING GAUSSIAN INTEGRAL
VAN DER WAALS FLUID
$W_{ij} = W(r_{ij})$, $r_{ij} = |\vec{r}_i - \vec{r}_j|$
• INTERACTING GAS
$H = \sum_i \frac{\vec{p}_i^2}{2m} + \sum_{ij} W_{ij}$

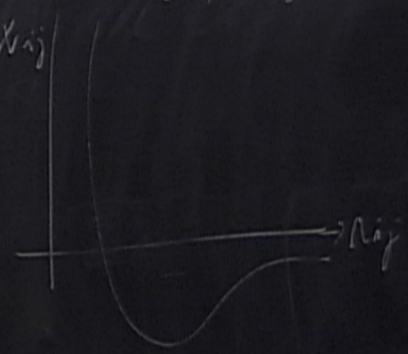
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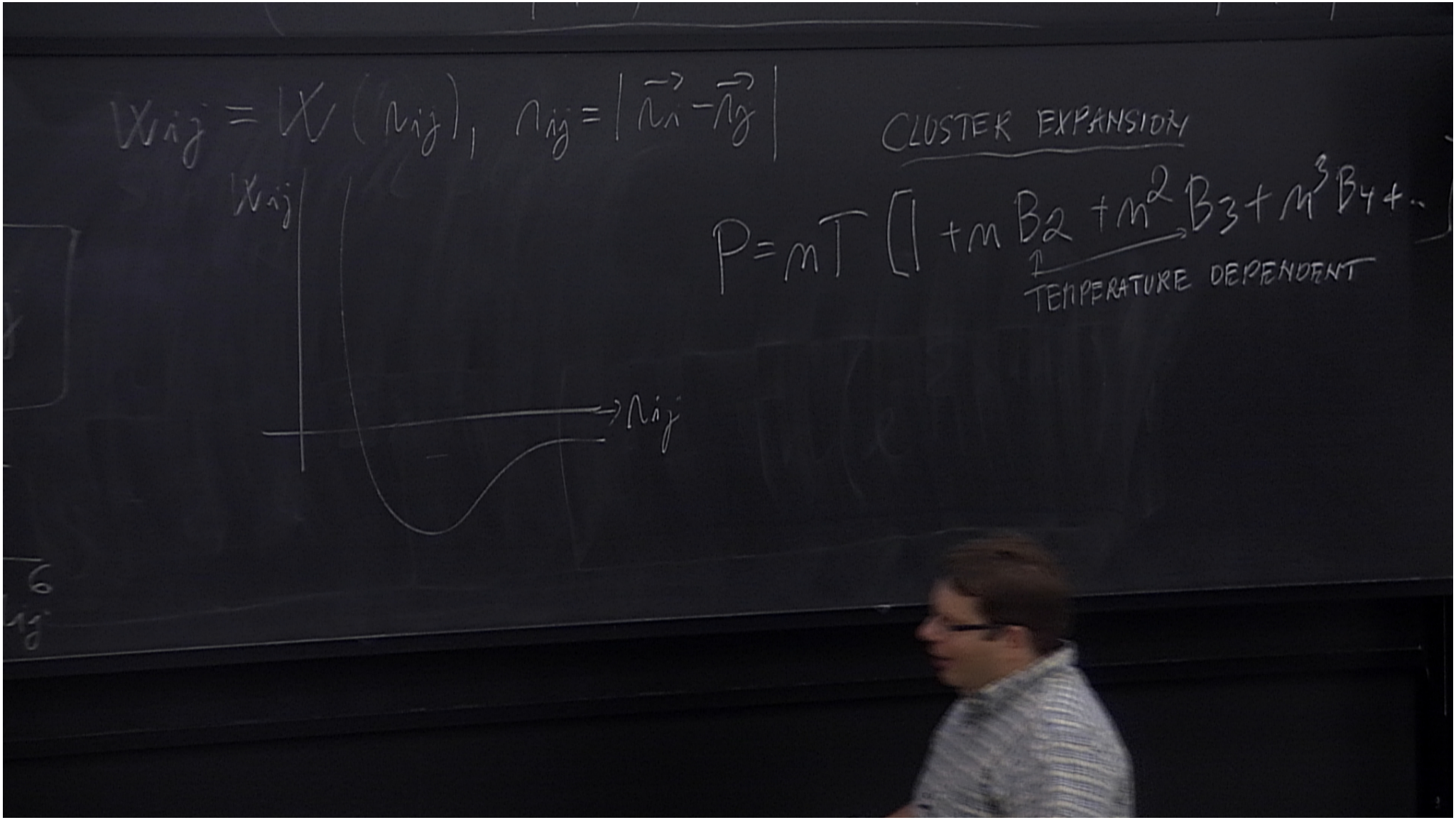
- INTERACTING GAS

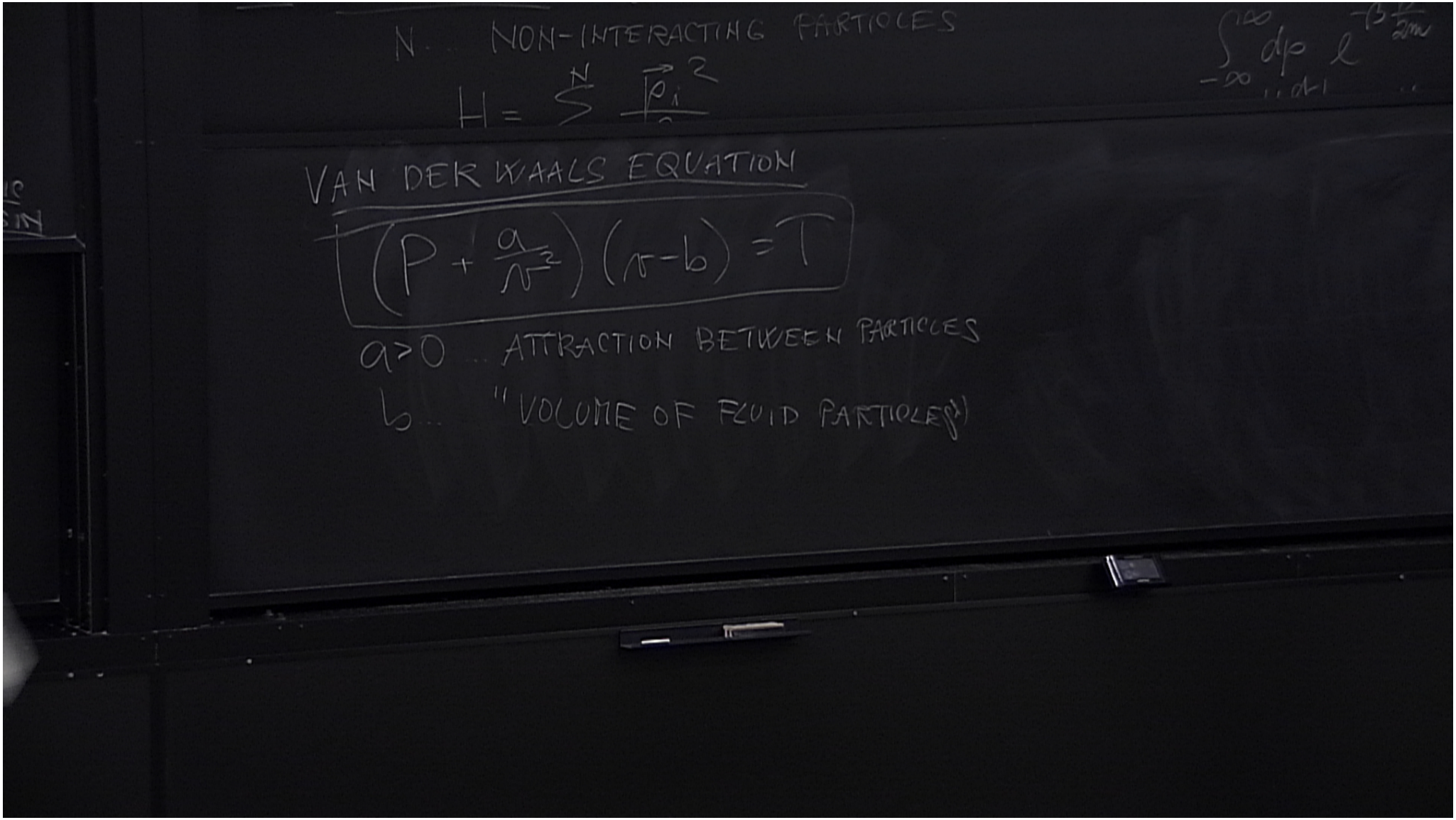
$$H = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \sum_{ij} W_{ij}$$



LENNARD-JONES POTENTIAL

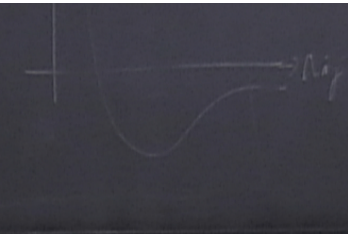
$$W_{ij} \propto \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}}$$


$V_{ij} = V(r_{ij})$, $r_{ij} = |\vec{r}_i - \vec{r}_j|$
CLUSTER EXPANSION
$P = nT\left[1 + nB_2 + n^2 B_3 + n^3 B_4 + \ldots\right.$
TEMPERATURE DEPENDENT
V_{ij}
r_{ij}


N ... NON-INTERACTING PARTICLES
$H = \sum^{N} \frac{\vec{p}_i^{\,2}}{2m}$
$\int_{-\infty}^{\infty} dp\, e^{-\beta \frac{p^2}{2m}}$
VAN DER WAALS EQUATION
$\left(P + \frac{a}{v^2}\right)(v-b) = T$
$a > 0$ ... ATTRACTION BETWEEN PARTICLES
b ... "VOLUME OF FLUID PARTICLES"

LENNARD-JONES POTENTIAL

$$W_{ij} \propto \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}}$$



EX: IDEAL GAS — d - SPACETIME DIMENSION

N NON-INTERACTING PARTICLES

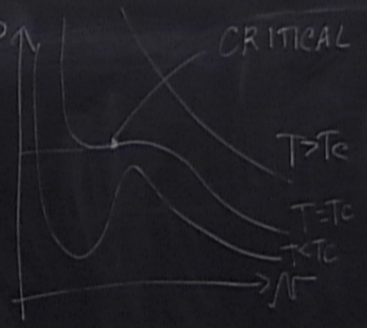
USING GAUSSIAN INTEGRAL ... $\int e^{-x^2} \Gamma_n$

VAN DER WAALS EQUATION

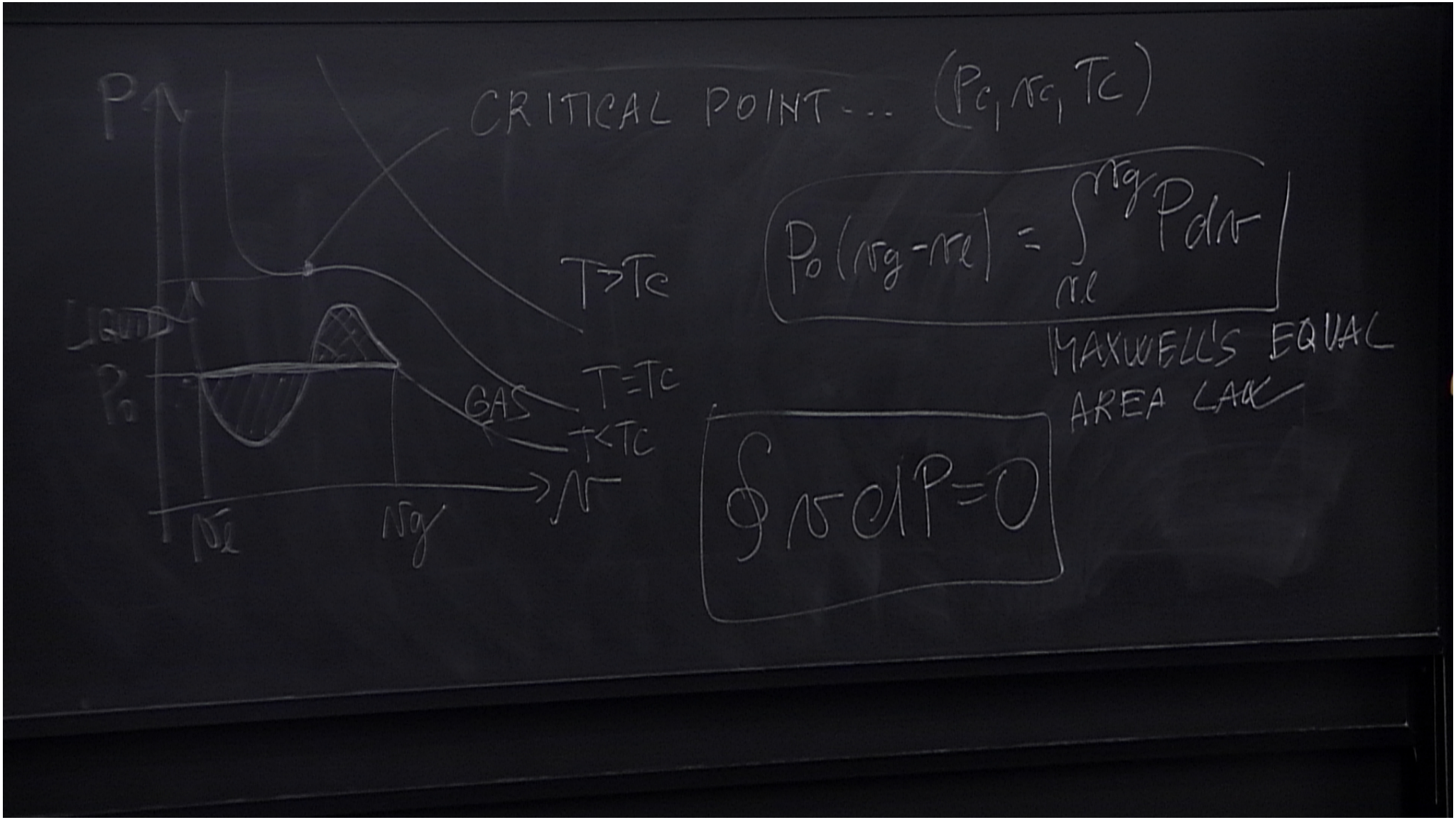
$$\left(P + \frac{a}{v^2}\right)(v - b) = T$$

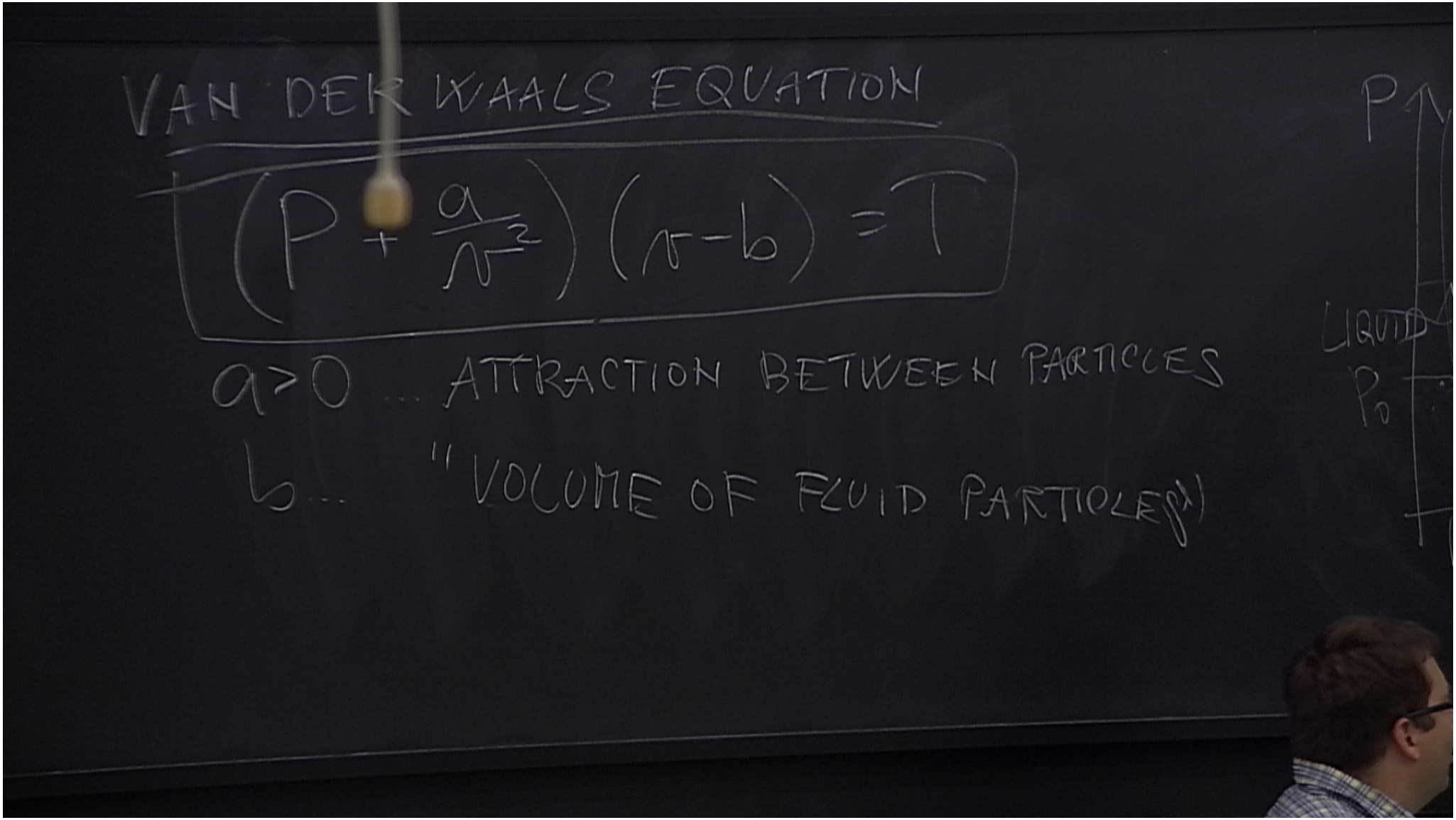
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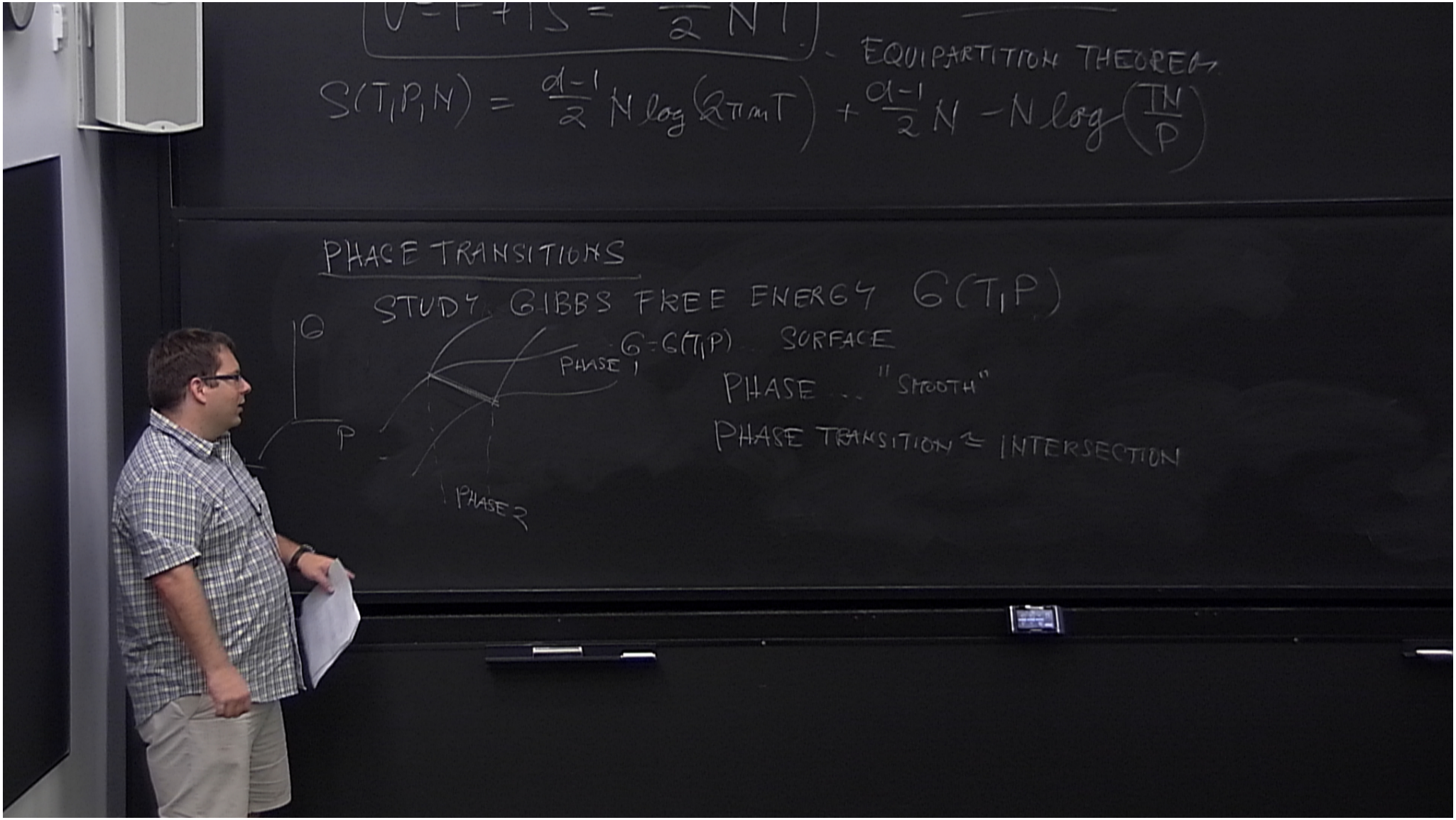
b "VOLUME OF FLUID PARTICLES"

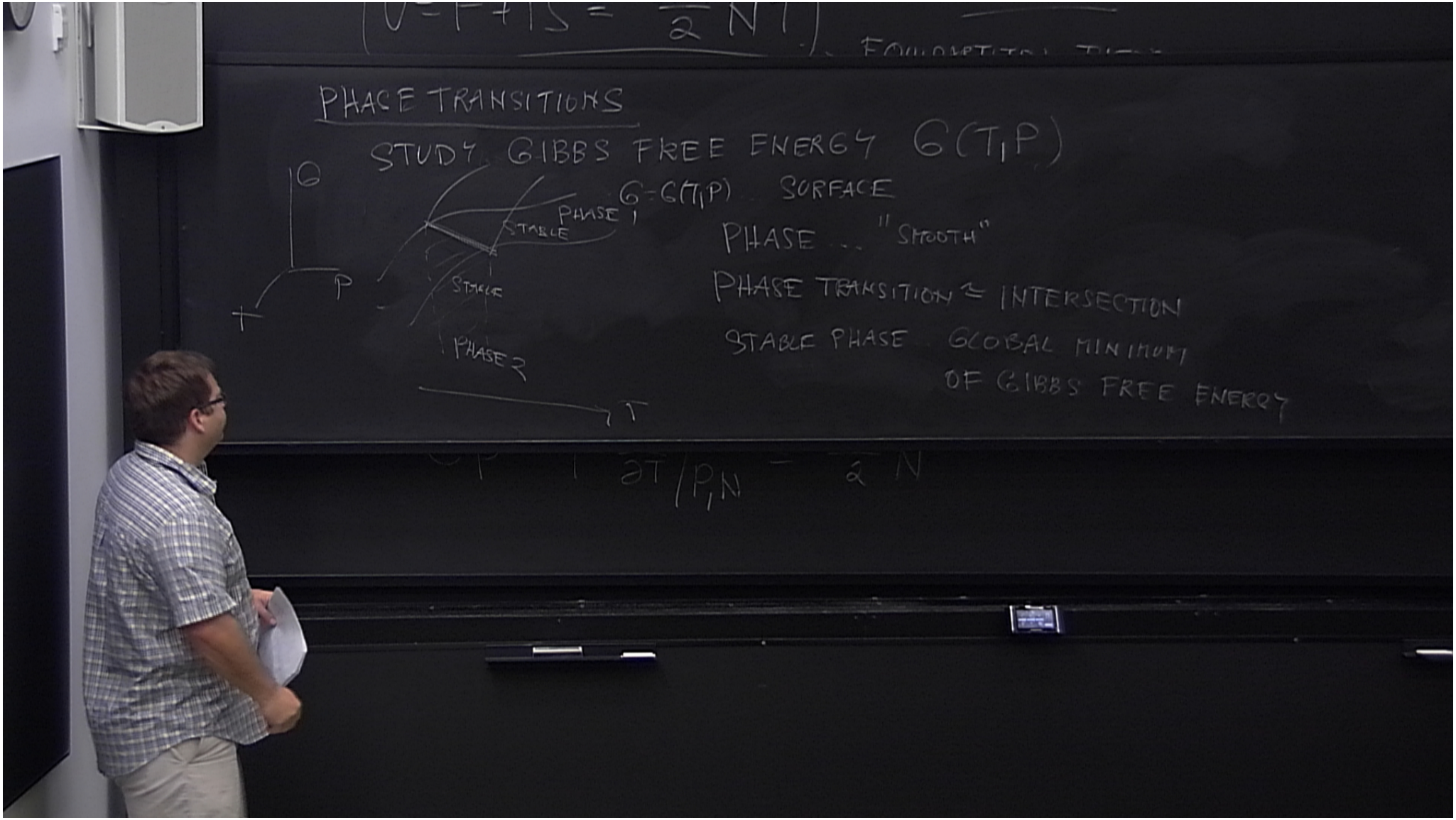


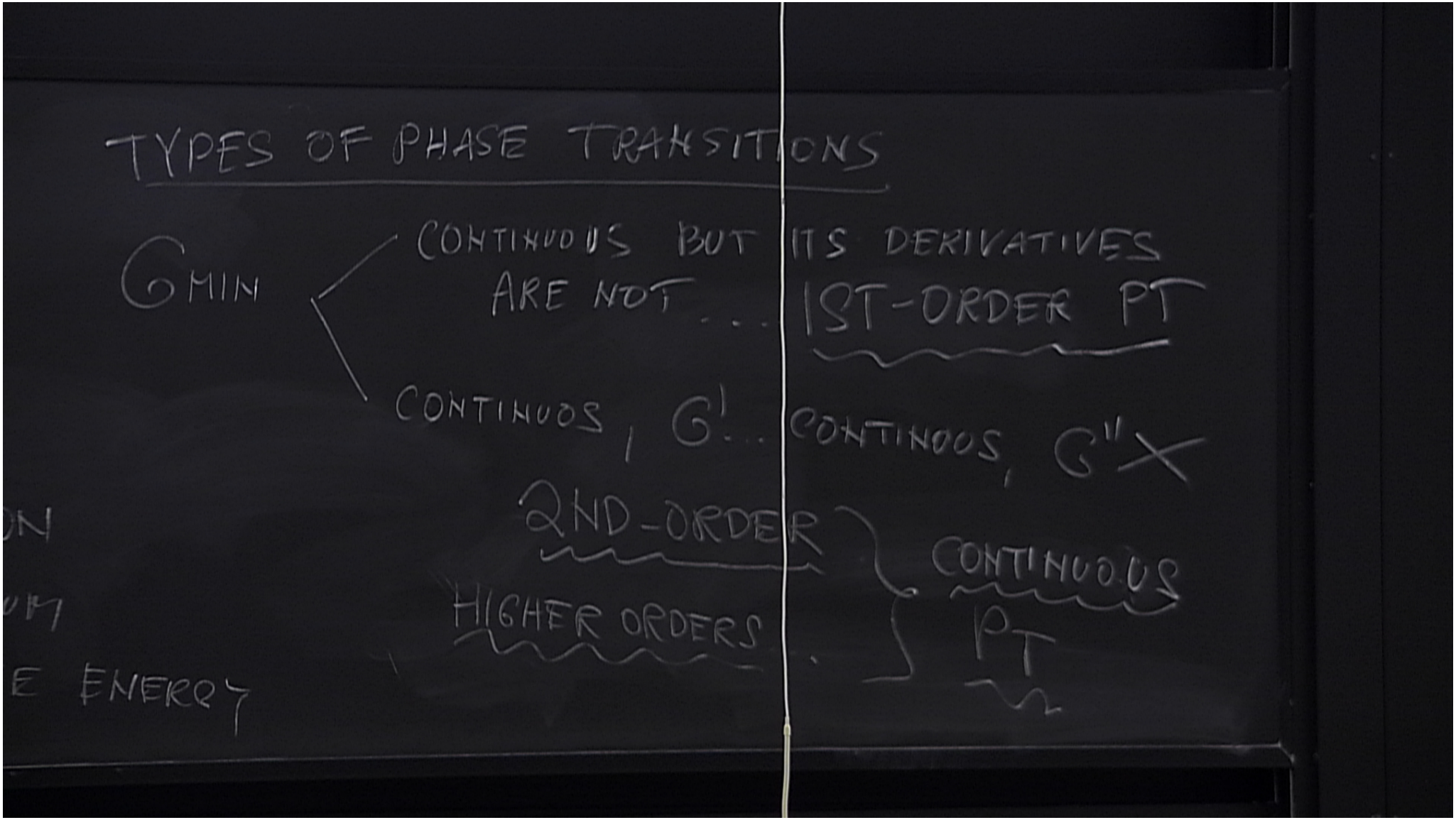
CRITICAL POINT ... (P_c, v_c, T_c)

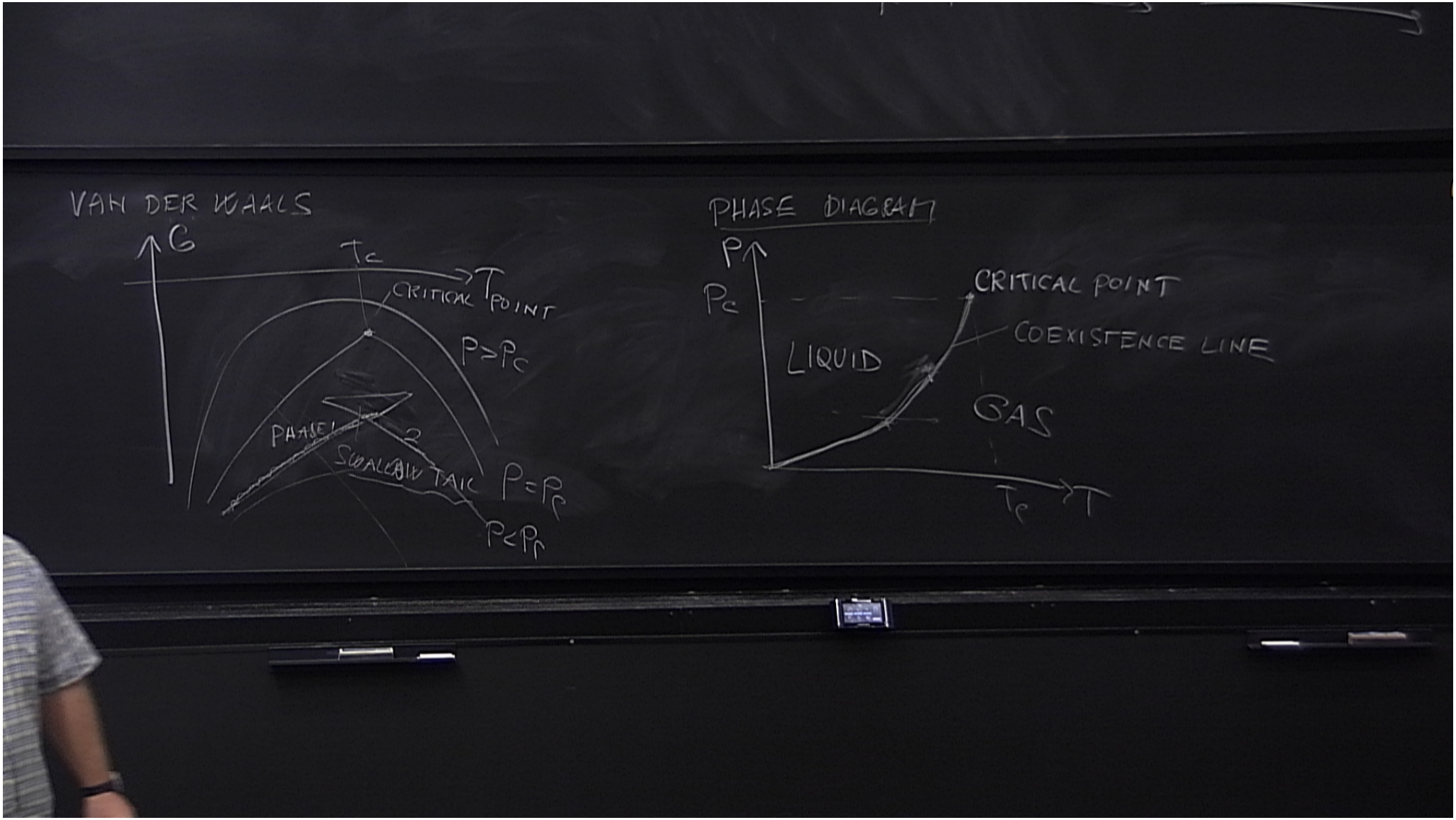

P
CRITICAL POINT ... (P_c, ν_c, T_c)
T>Tc
$P_0(\nu_g - \nu_\ell) = \int_{\nu_\ell}^{\nu_g} P\,d\nu$
MAXWELL'S EQUAL AREA LAW
LIQUID
P_0
GAS
T=Tc
T<Tc
$\oint \nu\,dP = 0$
ν_ℓ
ν_g
ν

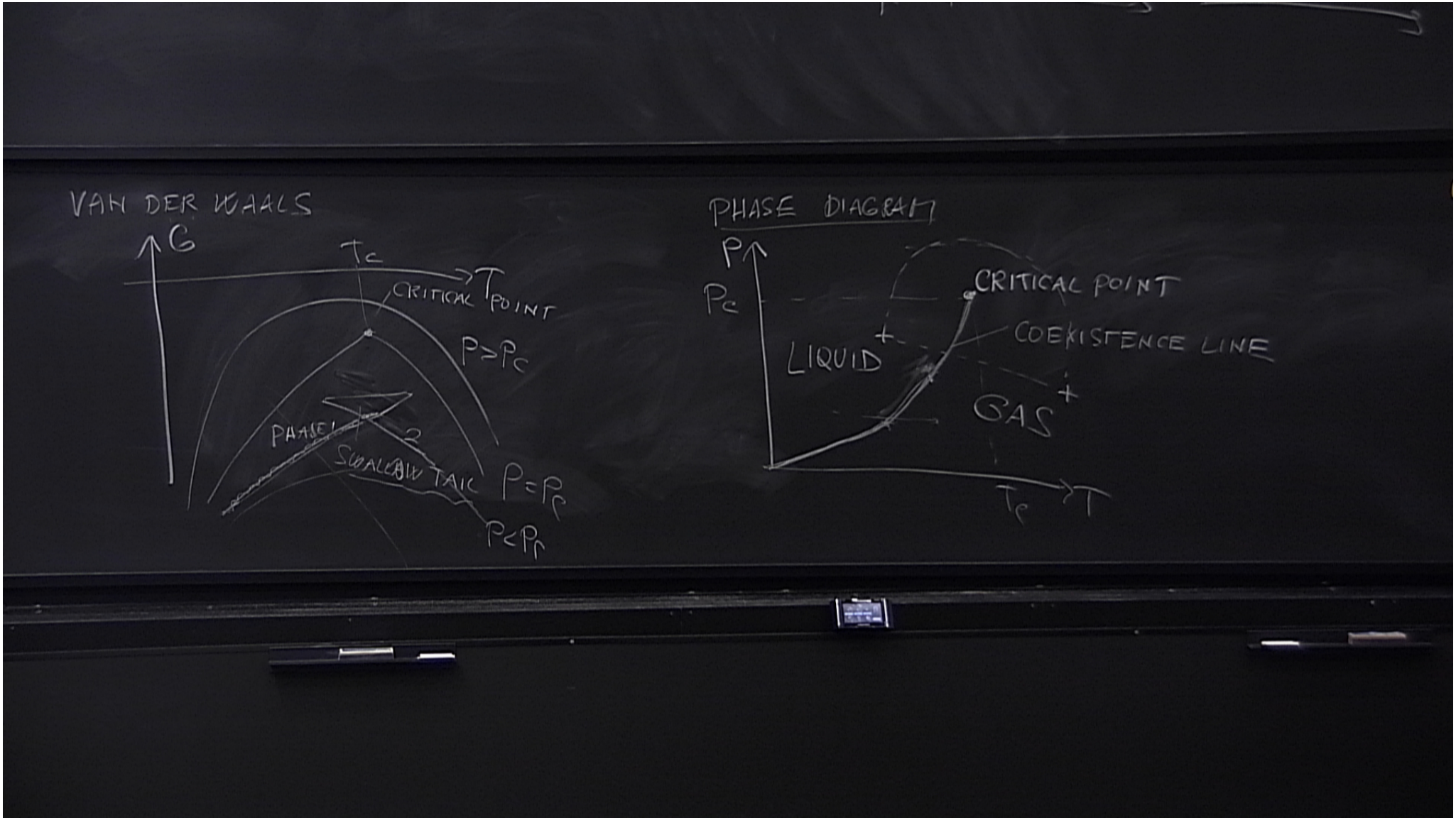

VAN DER WAALS EQUATION
$\left(P + \frac{a}{v^2}\right)(v - b) = T$
$a > 0$ ... ATTRACTION BETWEEN PARTICLES
b ... "VOLUME OF FLUID PARTICLES"
P
LIQUID
P_0


$U = F + TS = \frac{d}{2} NT$
EQUIPARTITION THEOREM
$S(T,P,N) = \frac{d-1}{2} N \log\left(2\pi m T\right) + \frac{d-1}{2} N - N \log\left(\frac{N}{P}\right)$
PHASE TRANSITIONS
STUDY GIBBS FREE ENERGY $G(T,P)$
G
P
$G = G(T,P)$ SURFACE
PHASE 1
PHASE 2
PHASE ... "SMOOTH"
PHASE TRANSITION $\rightleftharpoons$ INTERSECTION

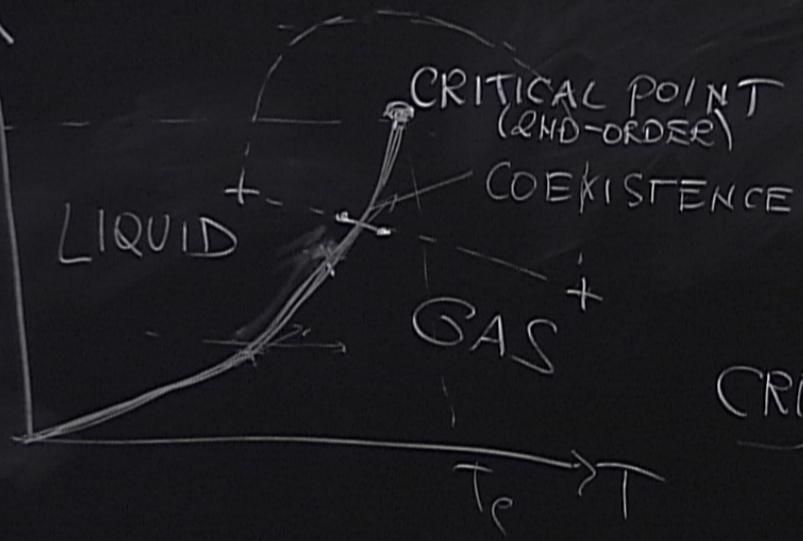

PHASE TRANSITIONS
STUDY GIBBS FREE ENERGY G(T,P)
G
G=G(T,P) SURFACE
PHASE 1
STABLE
PHASE ... "SMOOTH"
P
STABLE
PHASE TRANSITION ≅ INTERSECTION
PHASE 2
STABLE PHASE GLOBAL MINIMUM
OF GIBBS FREE ENERGY
T


TYPES OF PHASE TRANSITIONS
G MIN
CONTINUOUS BUT ITS DERIVATIVES ARE NOT...
1ST-ORDER PT
CONTINUOS, G'...
CONTINOOS, G'' X
2ND-ORDER
HIGHER ORDERS...
CONTINUOUS PT


VAN DER WAALS
G
Tc
T
CRITICAL POINT
P>Pc
PHASE 1
2
SUBALEAU TAIL
P=Pc
P<Pc
PHASE DIAGRAM
P
Pc
CRITICAL POINT
COEXISTENCE LINE
LIQUID
GAS
Tc
T


VAN DER WAALS
G
Tc
T
CRITICAL POINT
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P=Pc
P<Pc
PHASE DIAGRAM
P
Pc
CRITICAL POINT
COEXISTENCE LINE
LIQUID
GAS
Tc
T

PHASE DIAGRAM



SLOPE OF COEXISTENCE LINE

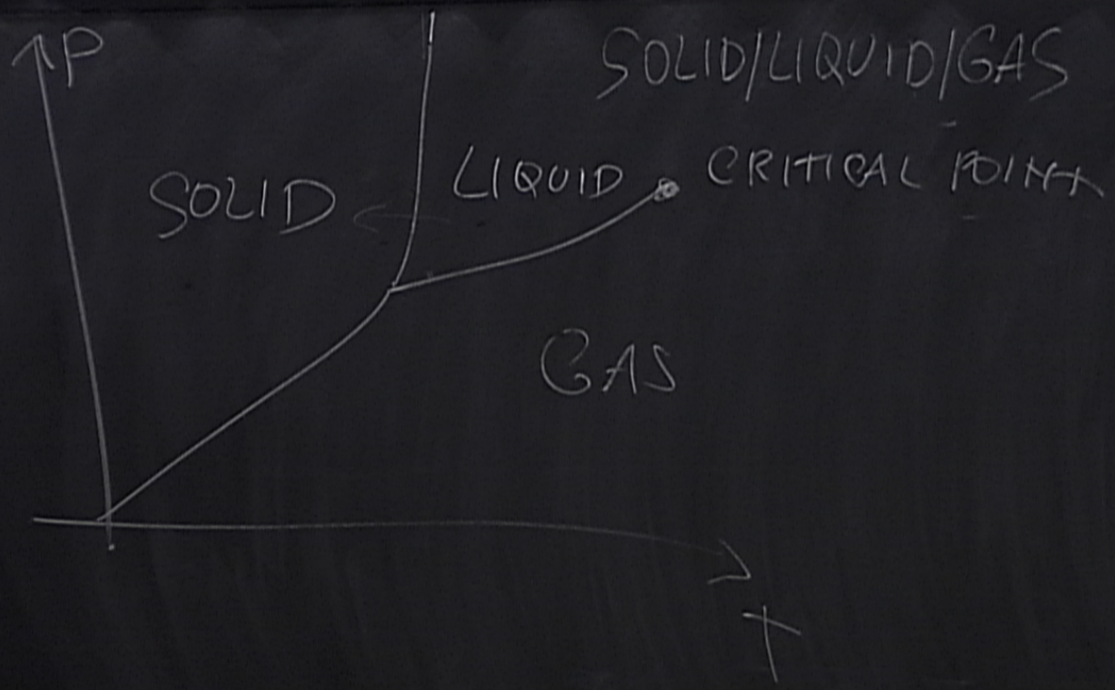
$$\left.\frac{dP}{dT}\right|_{COEX} = \frac{\Delta S}{\Delta V} = \frac{S_G - S_L}{V_G - V_L}$$

CLAUSIUS-CLAPEYRON, ... 1ST-ORDER

CRITICAL POINT

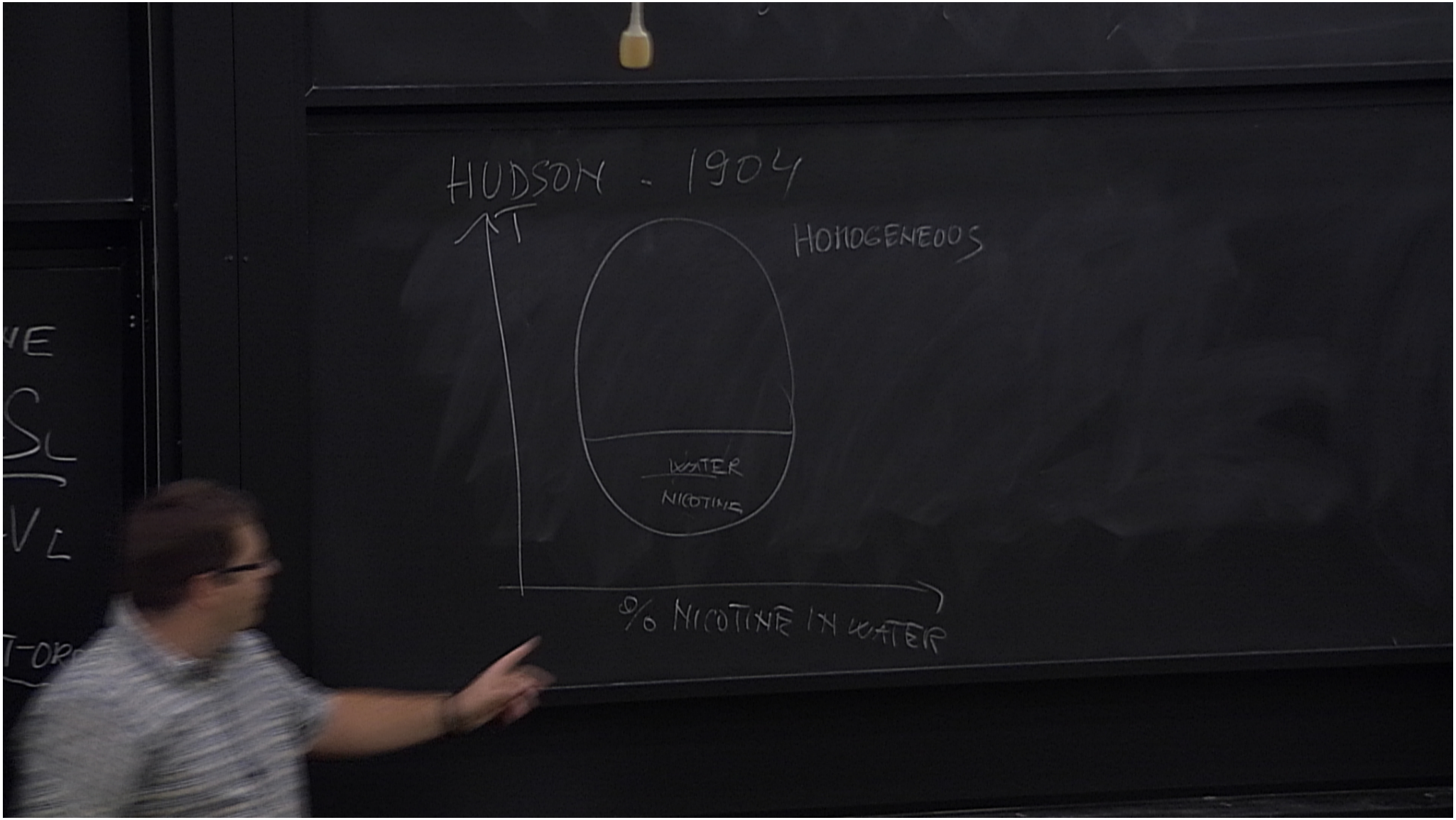
a>0 ... ATTRACTION BETWEEN PARTICLES

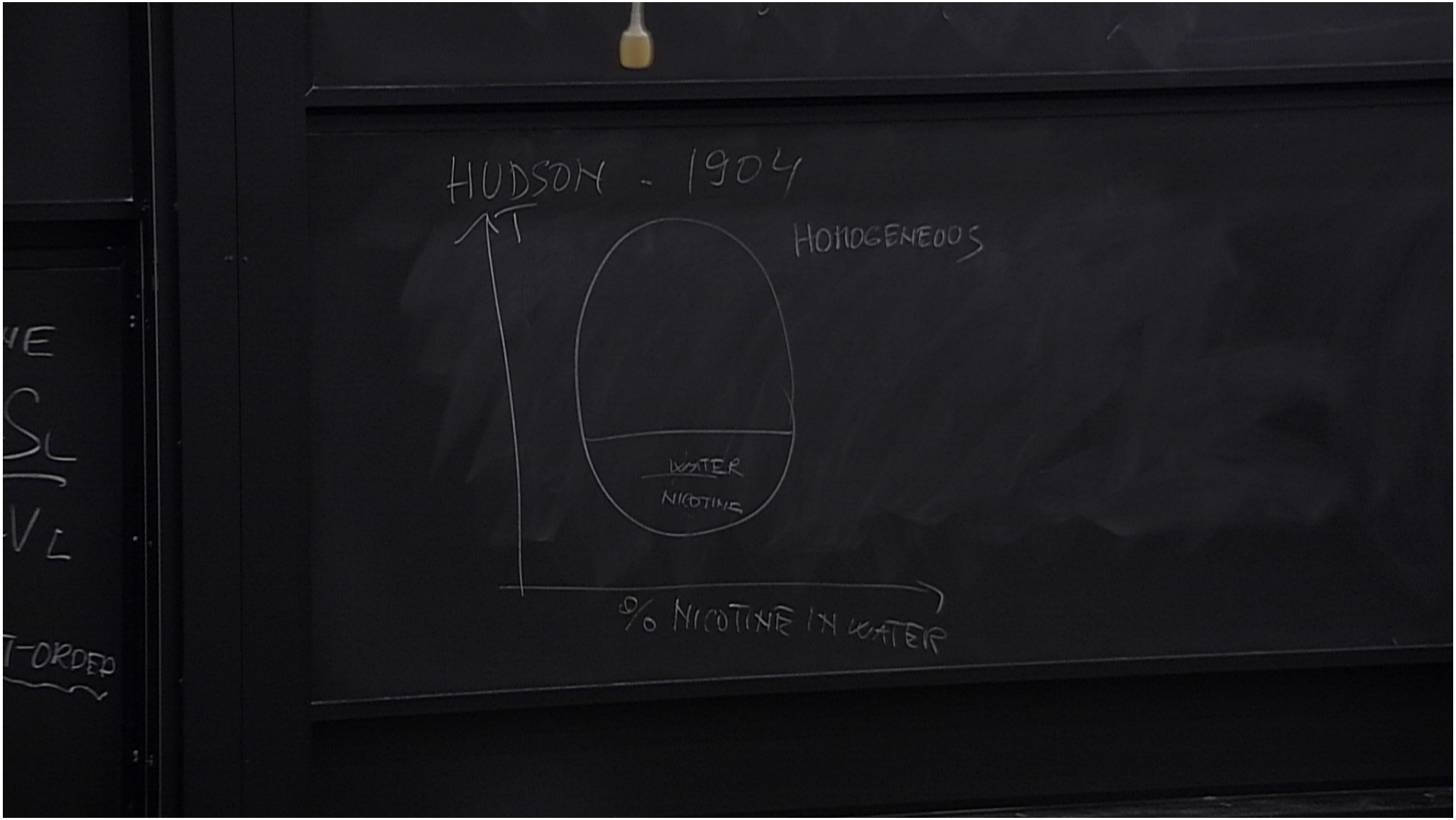
b ... "VOLUME OF FLUID PARTICLES"



- REENTRANT PHASE TRANSITION

DEF: A SYSTEM UNDERGOES RPT IF A MONOTONIC VARIATION OF ANY TD QUANTITY RESULTS IN TWO PHASE TRANSITIONS SO THAT THE FINAL STATE IS MACROSCOPICALLY SIMILAR TO INITIAL STATE.


HUDSON - 1904
T
HOMOGENEOUS
WATER
NICOTINE
% NICOTINE IN WATER


HUDSON - 1904
T
HOMOGENEOUS
WATER
NICOTINE
% NICOTINE IN WATER