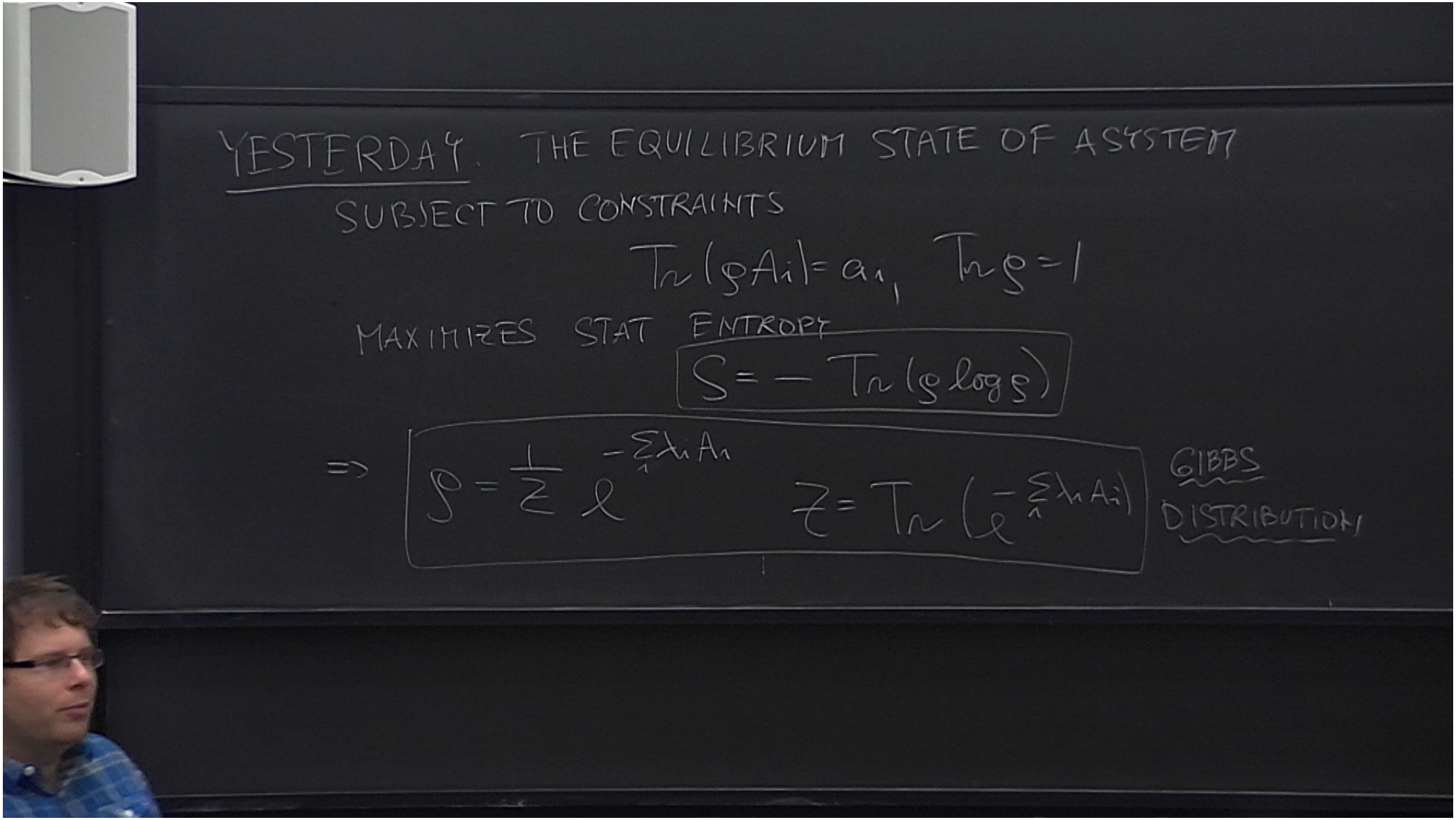
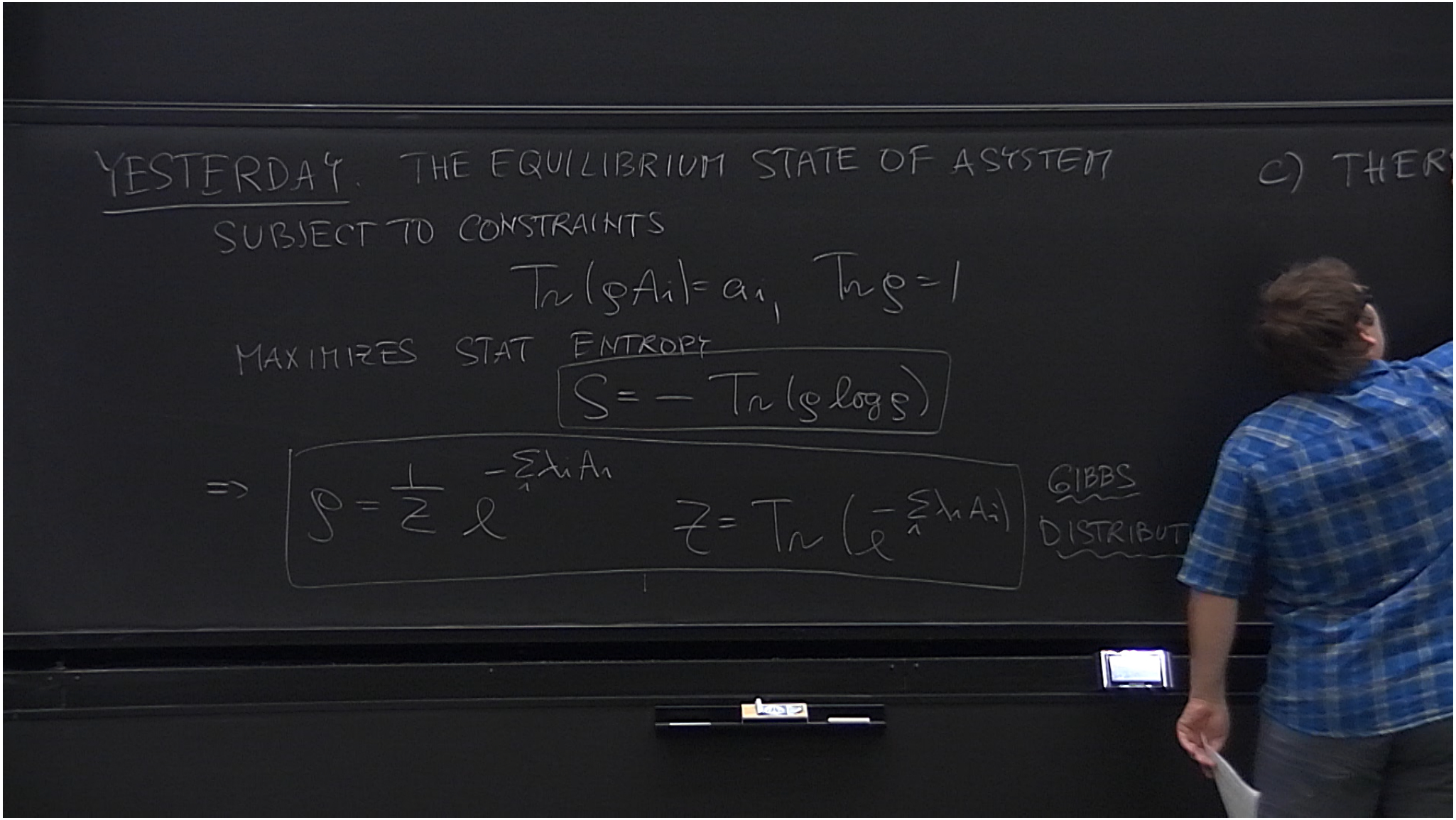
Title: PSI 17/18 - Statistical Mechanics - Lecture 3

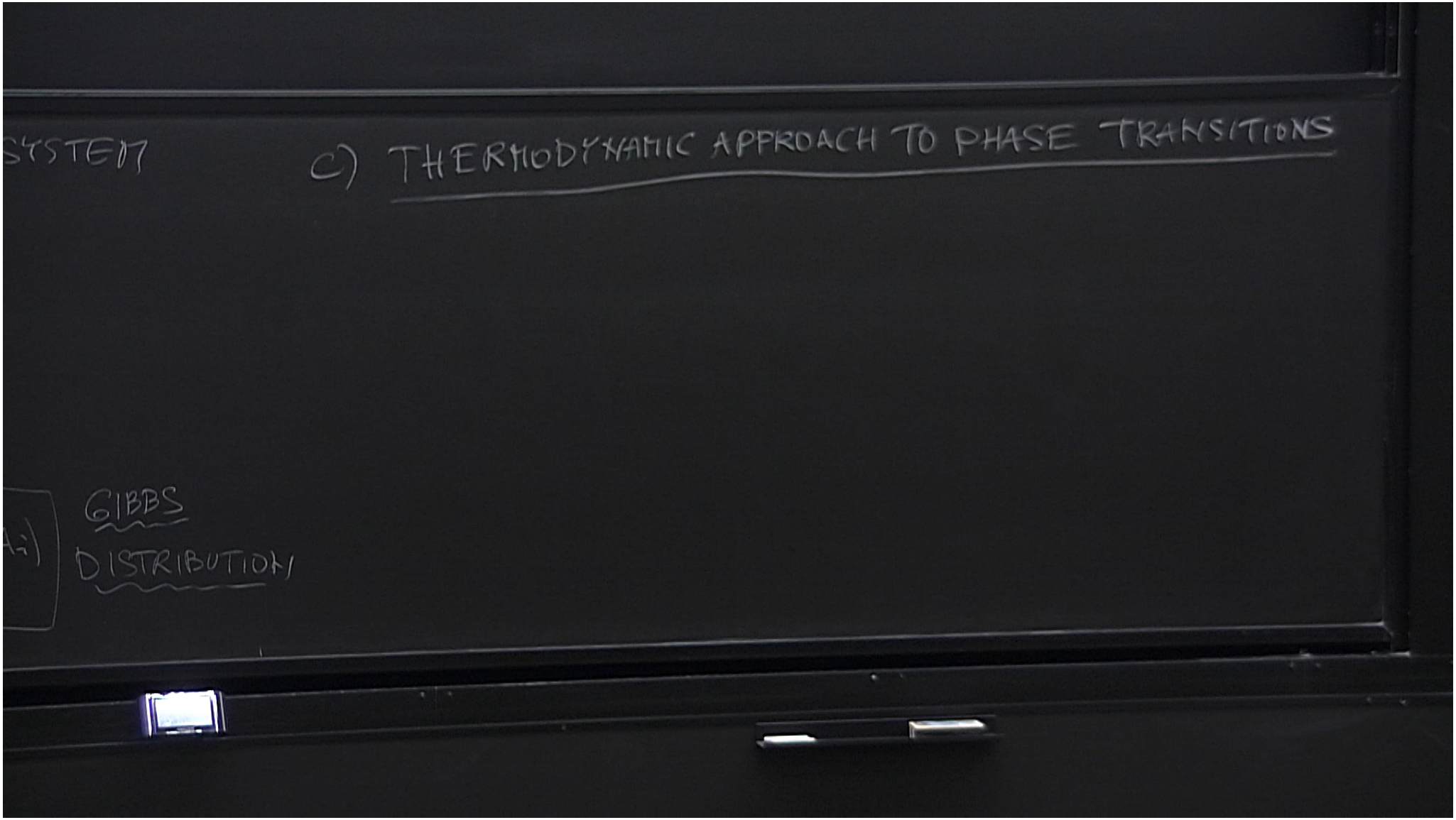
Date: Oct 12, 2017 10:45 AM

URL: http://pirsa.org/17100036

Abstract:


YESTERDAY. THE EQUILIBRIUM STATE OF A SYSTEM
SUBJECT TO CONSTRAINTS
$Tr(\rho A_i) = a_i, \quad Tr\rho = 1$
MAXIMIZES STAT ENTROPY
$S = -Tr(\rho \log \rho)$
$\Rightarrow \quad \rho = \frac{1}{Z} e^{-\sum_i \lambda_i A_i} \qquad Z = Tr\left(e^{-\sum_i \lambda_i A_i}\right)$
GIBBS DISTRIBUTION


YESTERDAY. THE EQUILIBRIUM STATE OF A SYSTEM
SUBJECT TO CONSTRAINTS
$\mathrm{Tr}(\rho A_i) = a_i, \quad \mathrm{Tr}\,\rho = 1$
MAXIMIZES STAT ENTROPY
$S = -\mathrm{Tr}(\rho \log \rho)$
$\Rightarrow \quad \rho = \frac{1}{Z} e^{-\sum \lambda_i A_i} \qquad Z = \mathrm{Tr}\left(e^{-\sum \lambda_i A_i}\right)$
GIBBS
DISTRIBUT


SYSTEM
C) THERMODYNAMIC APPROACH TO PHASE TRANSITIONS
GIBBS
DISTRIBUTION

SYSTEM

c) THERMODYNAMIC APPROACH TO PHASE TRANSITIONS

i) STATISTICAL MACHINERY AT WORK: IDEAL GAS

- GIVEN HAMILTONIAN H
- FIRST CALCULATE PARTITION FUNCTION

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

- CALCULATE FREE ENERGY

$$F = -T \log Z$$

GIBBS DISTRIBUTION

- FROM TDS $F = F(T, V, N)$

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}, \quad P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}$$

EXAMPLE . IDEAL GAS

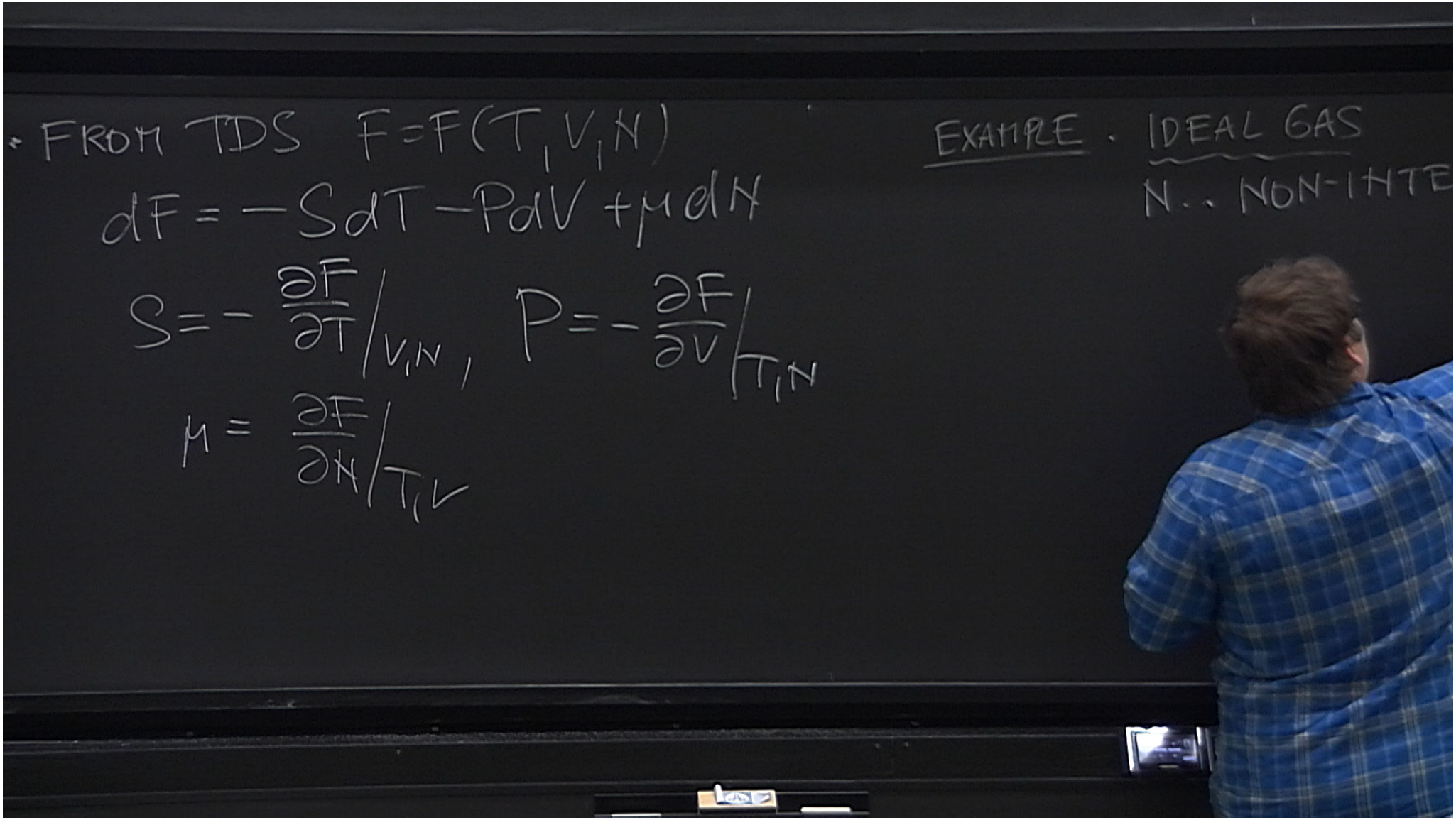
- FROM TDS $F = F(T, V, N)$

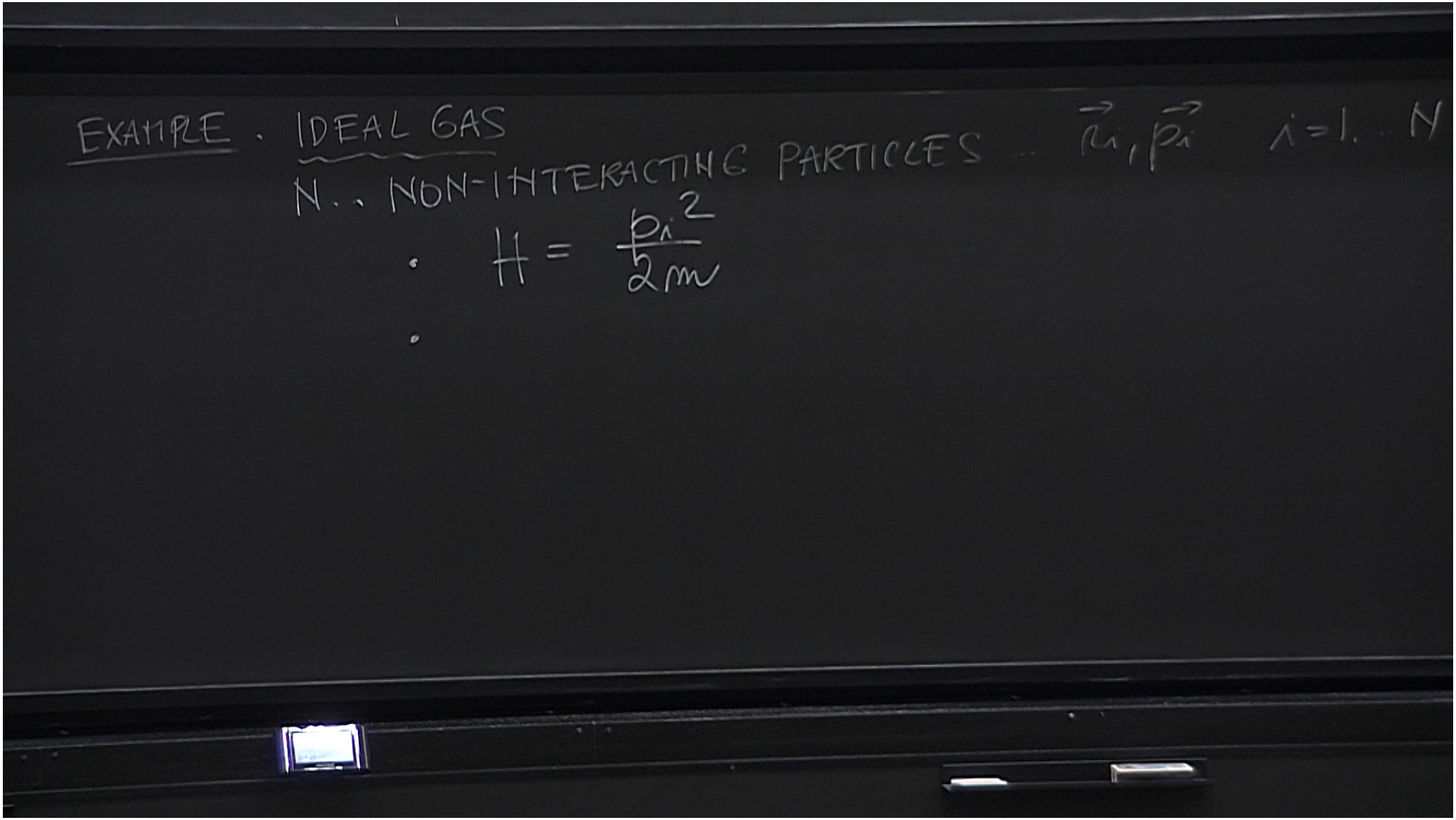
$$dF = -SdT - PdV + \mu dN$$

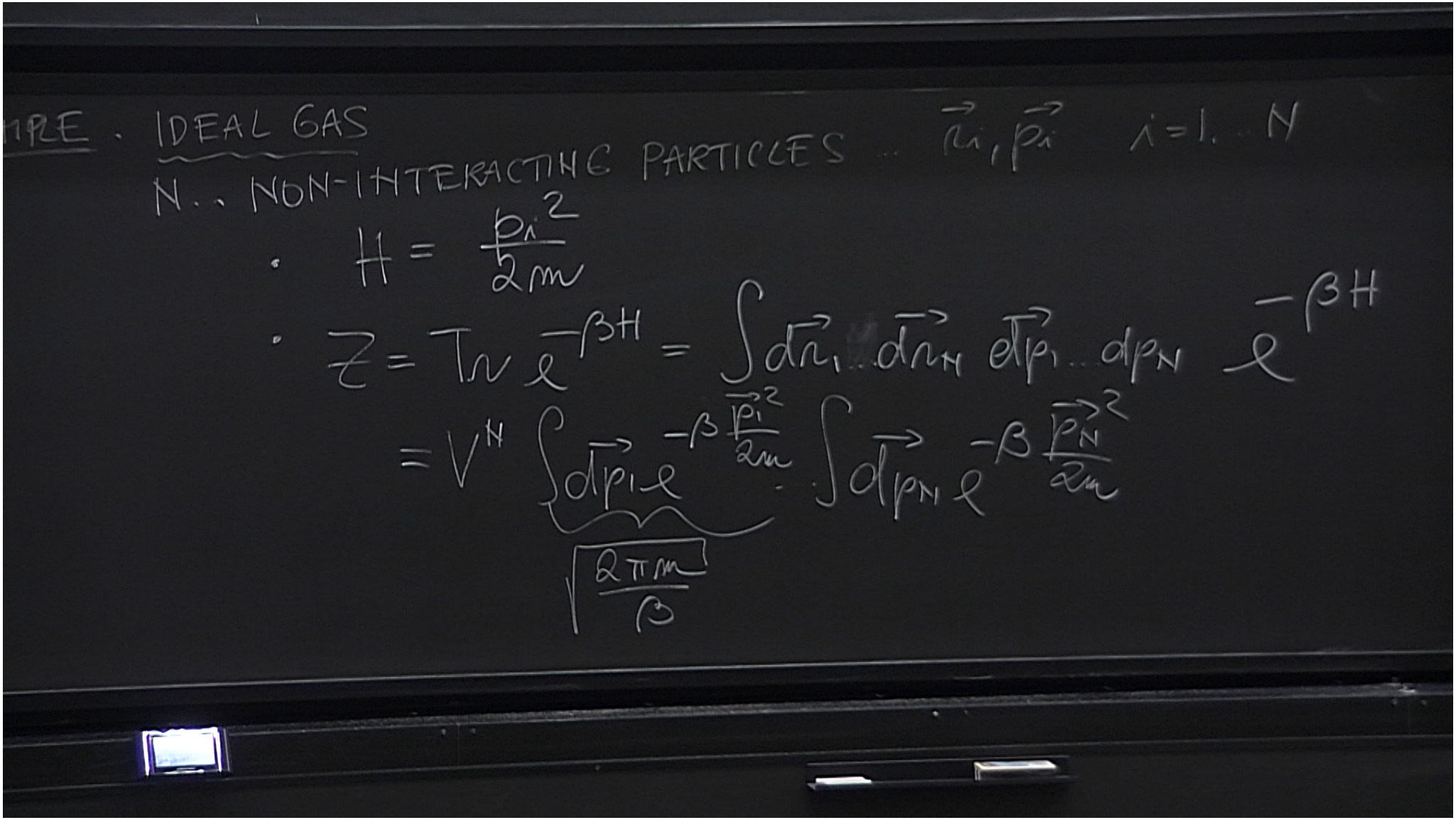
$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}, \quad P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$$

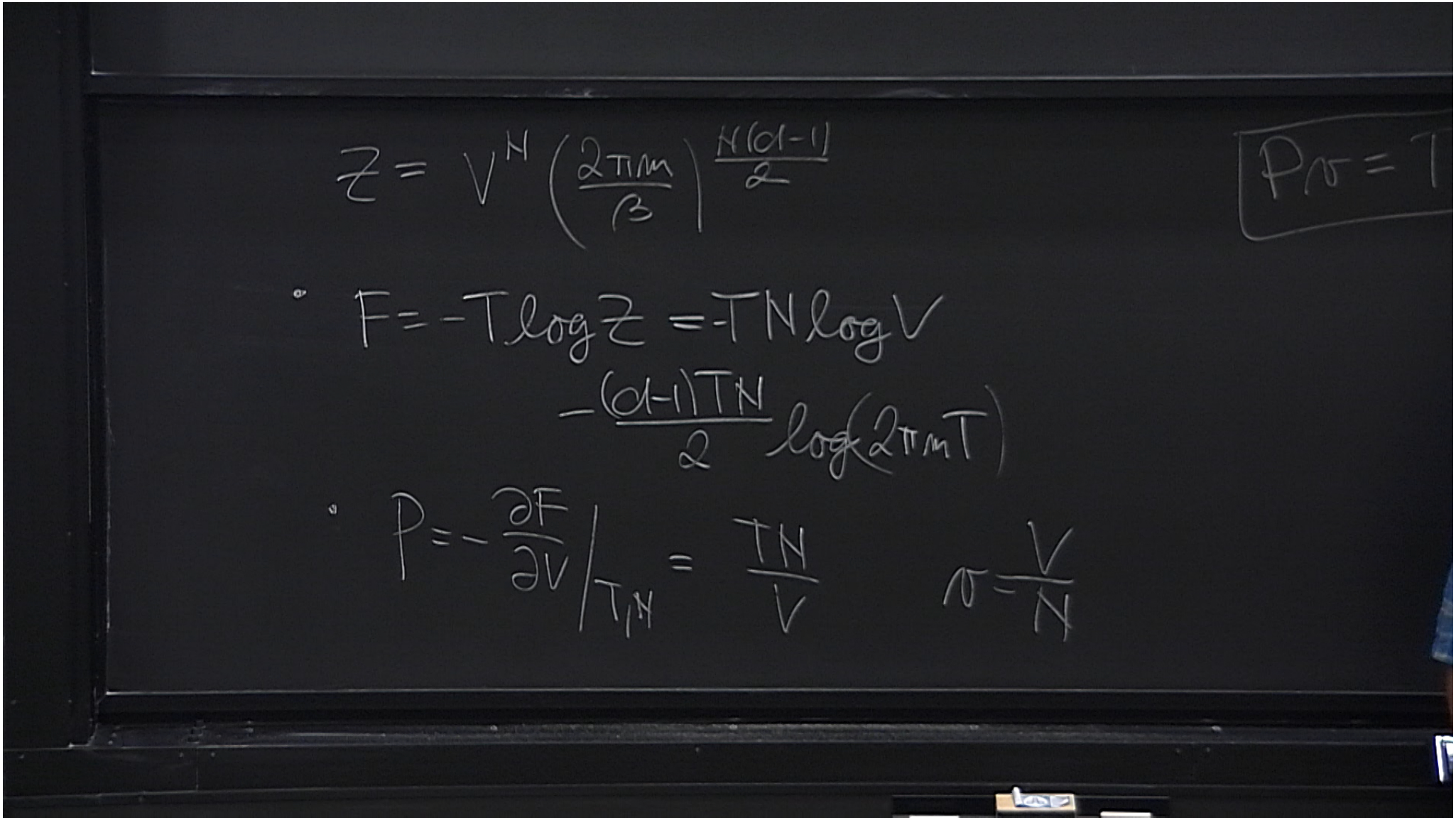
$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}$$

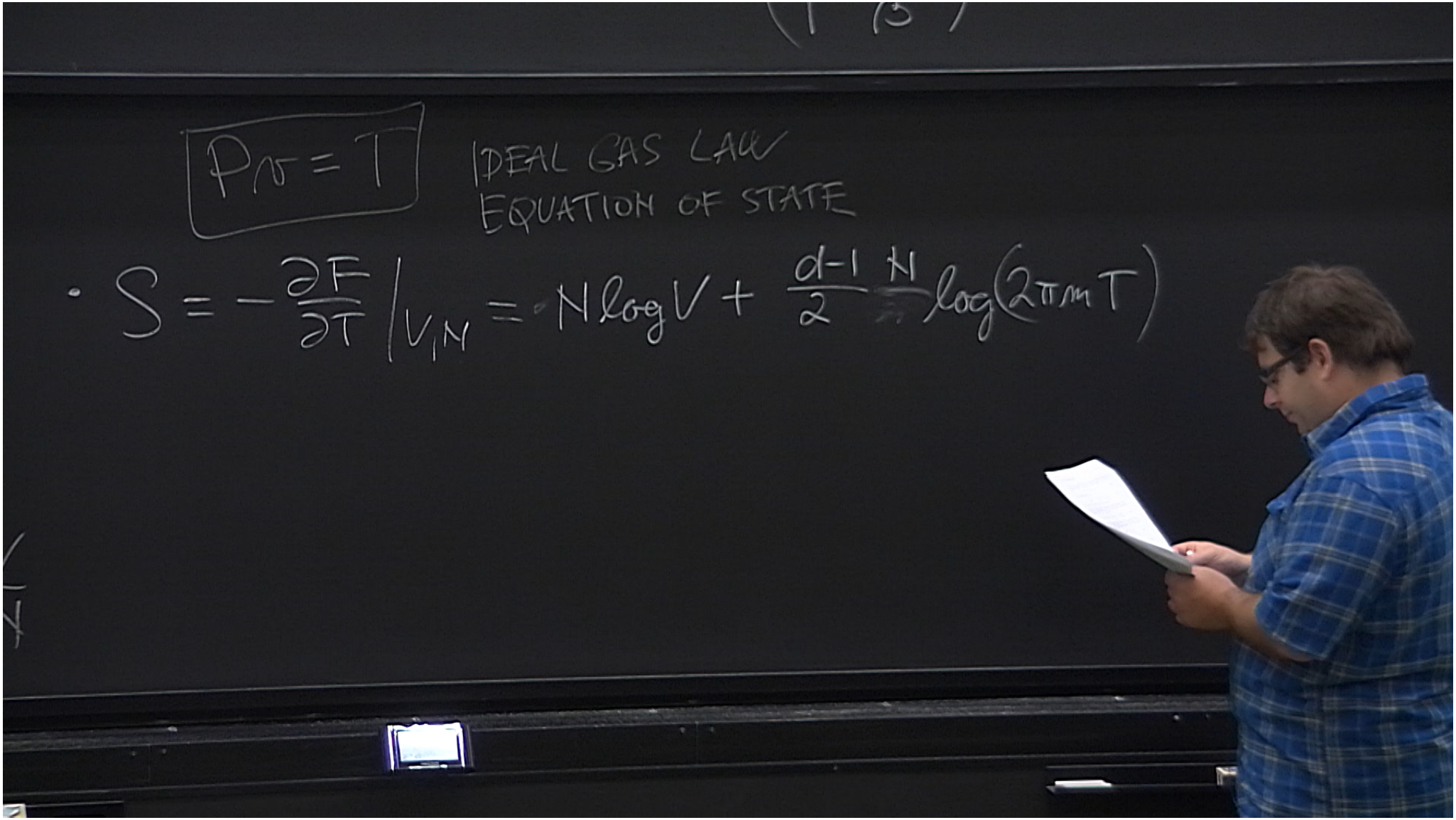
EXAMPLE . IDEAL GAS


FROM TDS $F = F(T, V, N)$
$dF = -SdT - PdV + \mu dN$
$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N}$, $P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$
$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V}$
EXAMPLE · IDEAL GAS
N.. NON-INTE


EXAMPLE . IDEAL GAS
N .. NON-INTERACTING PARTICLES .. $\vec{r}_i, \vec{p}_i$ $i = 1 .. N$
$H = \frac{p_i^2}{2m}$


IPLE . IDEAL GAS
N .. NON-INTERACTING PARTICLES .. $\vec{r}_i, \vec{p}_i$ $i = 1 \dots N$
$H = \frac{p_i^2}{2m}$
$Z = \mathrm{Tr}\, e^{-\beta H} = \int d\vec{r}_1 \dots d\vec{r}_N \, d\vec{p}_1 \dots d\vec{p}_N \, e^{-\beta H}$
$= V^N \int d\vec{p}_1 e^{-\beta \frac{\vec{p}_1^2}{2m}} \dots \int d\vec{p}_N e^{-\beta \frac{\vec{p}_N^2}{2m}}$
$\sqrt{\frac{2\pi m}{\beta}}$

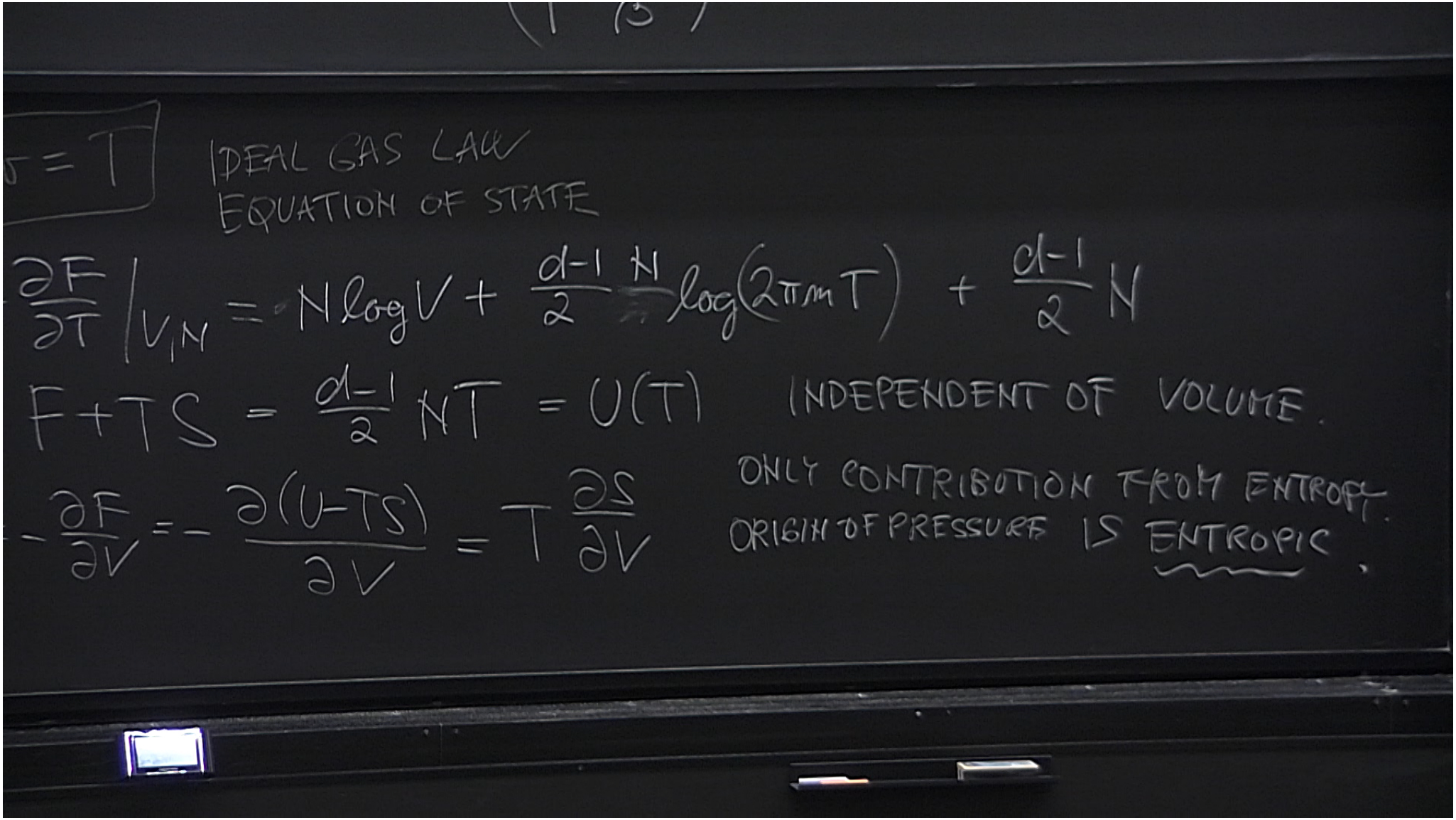

$Z = V^N \left(\frac{2\pi m}{\beta}\right)^{\frac{N(d-1)}{2}}$
$Pv = T$
$F = -T \log Z = -TN \log V - \frac{(d-1)TN}{2} \log(2\pi m T)$
$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{TN}{V}$
$v = \frac{V}{N}$

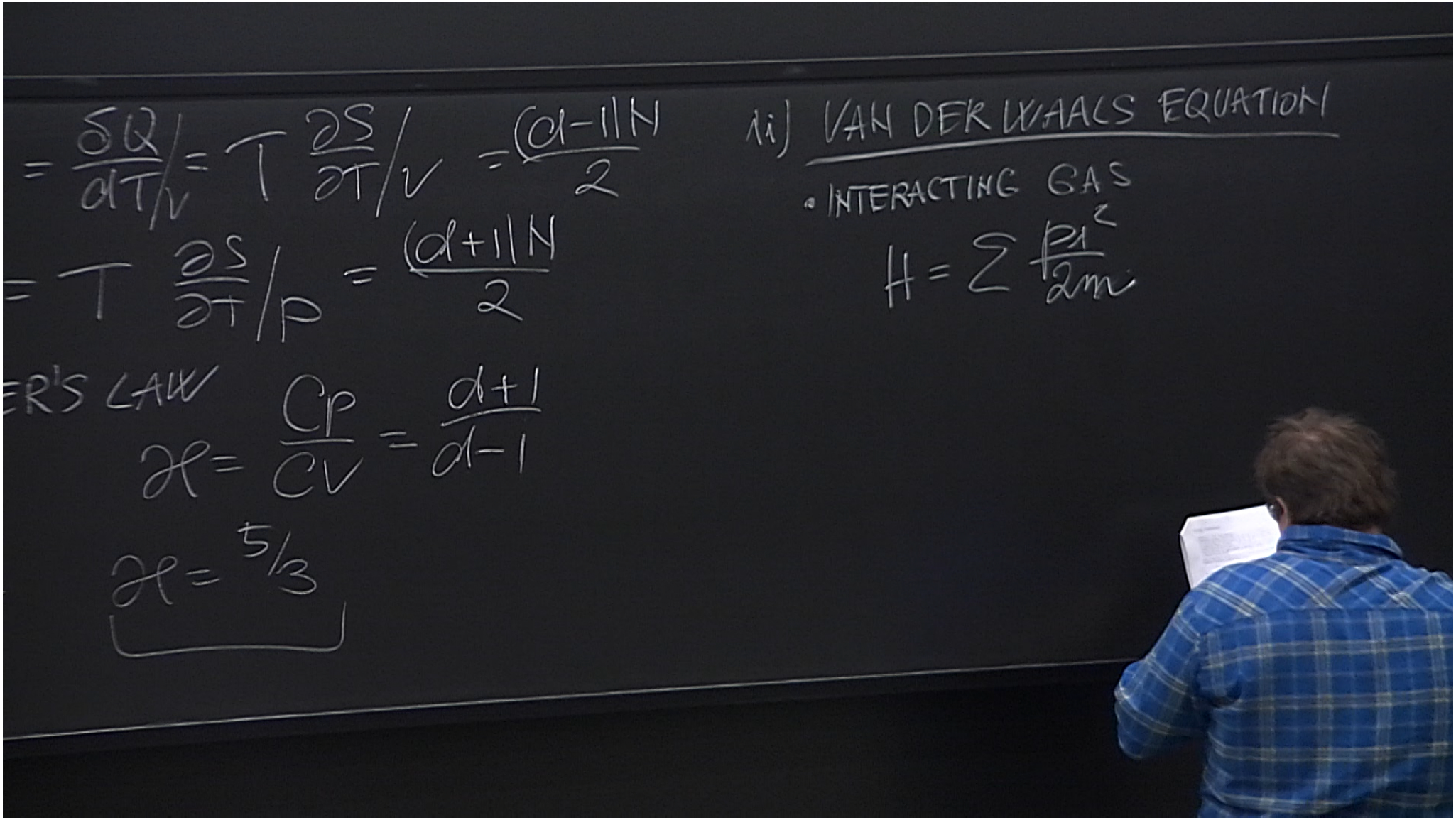

$PV = T$
IDEAL GAS LAW
EQUATION OF STATE
$S = -\frac{\partial F}{\partial T}\Big|_{V,N} = N \log V + \frac{d-1}{2} N \log(2\pi m T)$

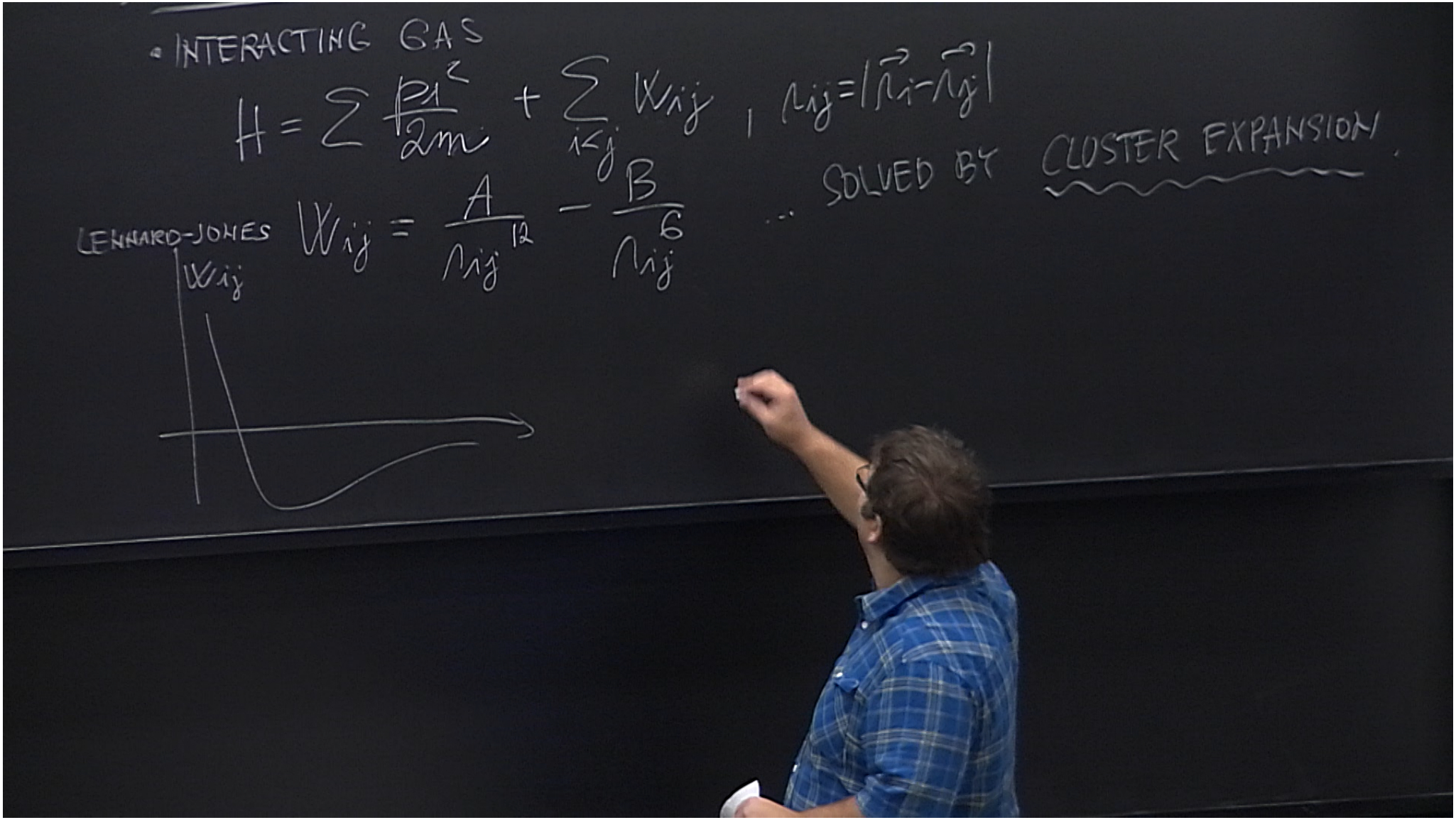
$PV = T$ IDEAL GAS LAW
EQUATION OF STATE

$$= -\frac{\partial F}{\partial T}\Big|_{V,N} = N \log V + \frac{d-1}{2} N \log(2\pi m T) + \frac{d-1}{2} N$$

$$U = F + TS = \frac{d-1}{2} NT = U(T)$$ INDEPENDENT OF VOLUME.


$P = T$
IDEAL GAS LAW
EQUATION OF STATE
$\left.\frac{\partial F}{\partial T}\right|_{V,N} = -N \log V + \frac{d-1}{2} N \log(2\pi m T) + \frac{d-1}{2} N$
$F + TS = \frac{d-1}{2} NT = U(T)$ INDEPENDENT OF VOLUME.
$-\frac{\partial F}{\partial V} = -\frac{\partial (U - TS)}{\partial V} = T \frac{\partial S}{\partial V}$
ONLY CONTRIBUTION FROM ENTROPY.
ORIGIN OF PRESSURE IS ENTROPIC.


$= \frac{\delta Q}{dT}\Big|_V = T\frac{\partial S}{\partial T}\Big|_V = \frac{(d-1)Nk}{2}$
$= T\frac{\partial S}{\partial T}\Big|_P = \frac{(d+1)Nk}{2}$
ER'S LAW
$\gamma = \frac{C_P}{C_V} = \frac{d+1}{d-1}$
$\gamma = 5/3$
ii) VAN DER WAALS EQUATION
• INTERACTING GAS
$H = \sum \frac{p_i^2}{2m_i}$


• INTERACTING GAS
$H = \sum \frac{p_i^2}{2m} + \sum_{i<j} W_{ij}$, $r_{ij} = |\vec{r}_i - \vec{r}_j|$
LENNARD-JONES $W_{ij} = \frac{A}{r_{ij}^{12}} - \frac{B}{r_{ij}^{6}}$
... SOLVED BY CLUSTER EXPANSION.
W_{ij}

- VAN DER WAALS EQ.

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

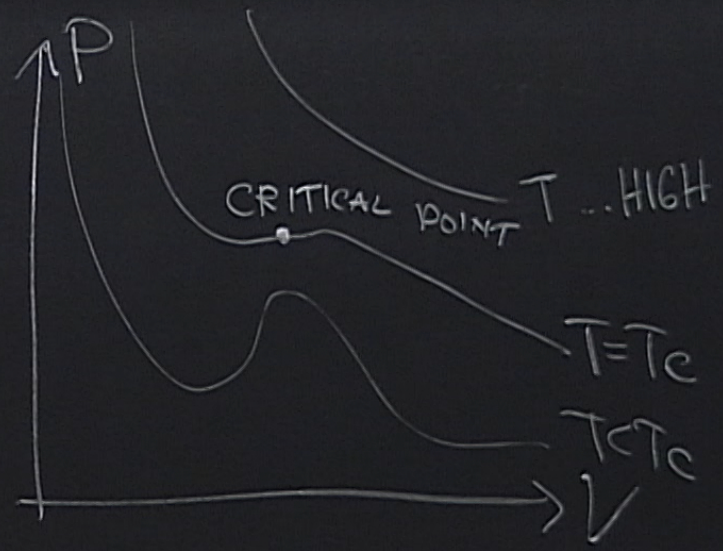
- $a > 0$ .. MEASURES ATTRACTION BETWEEN PARTICLES.
- b .. EXCLUDED VOLUME OF PARTICLES.

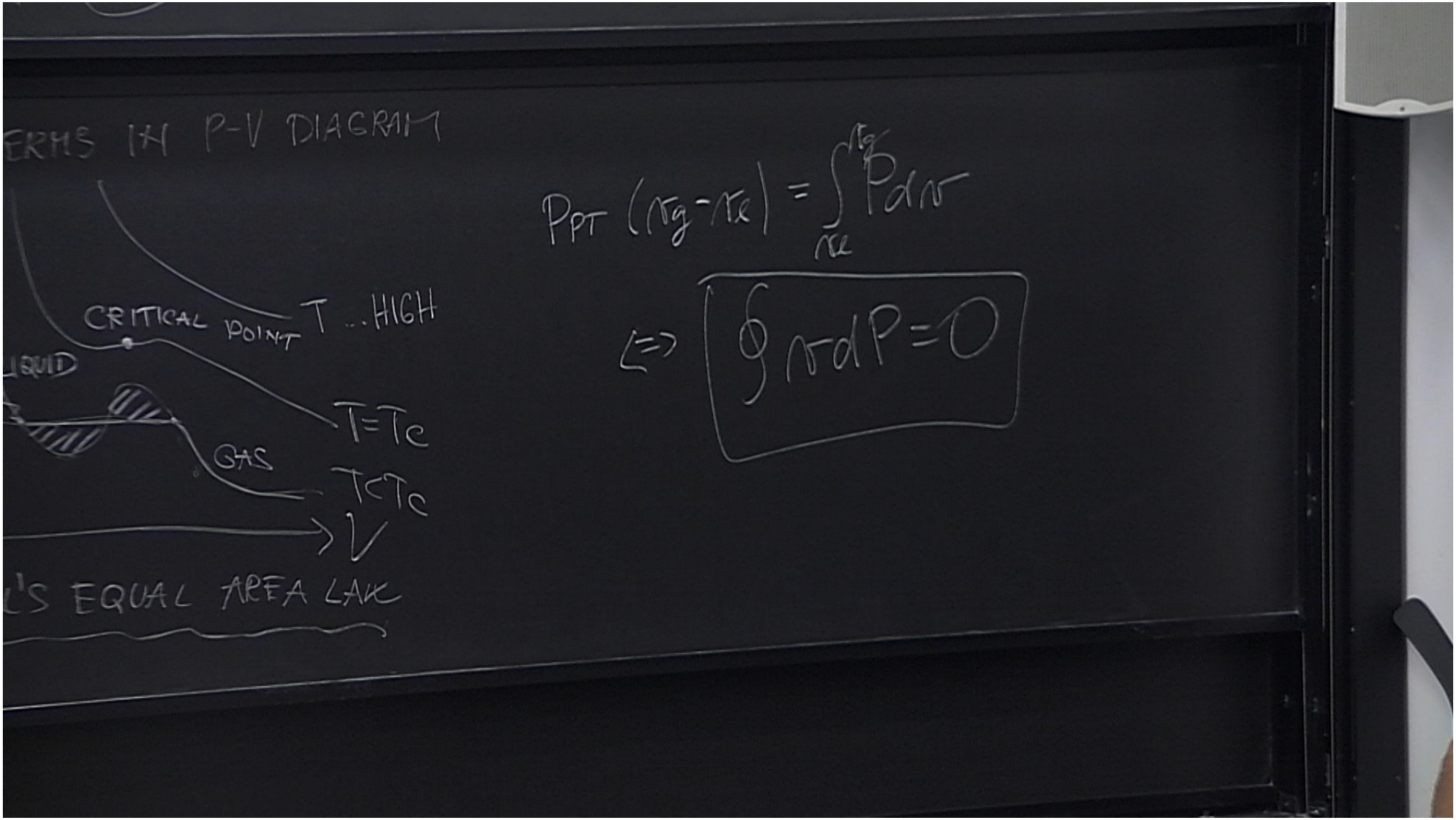
EQ.

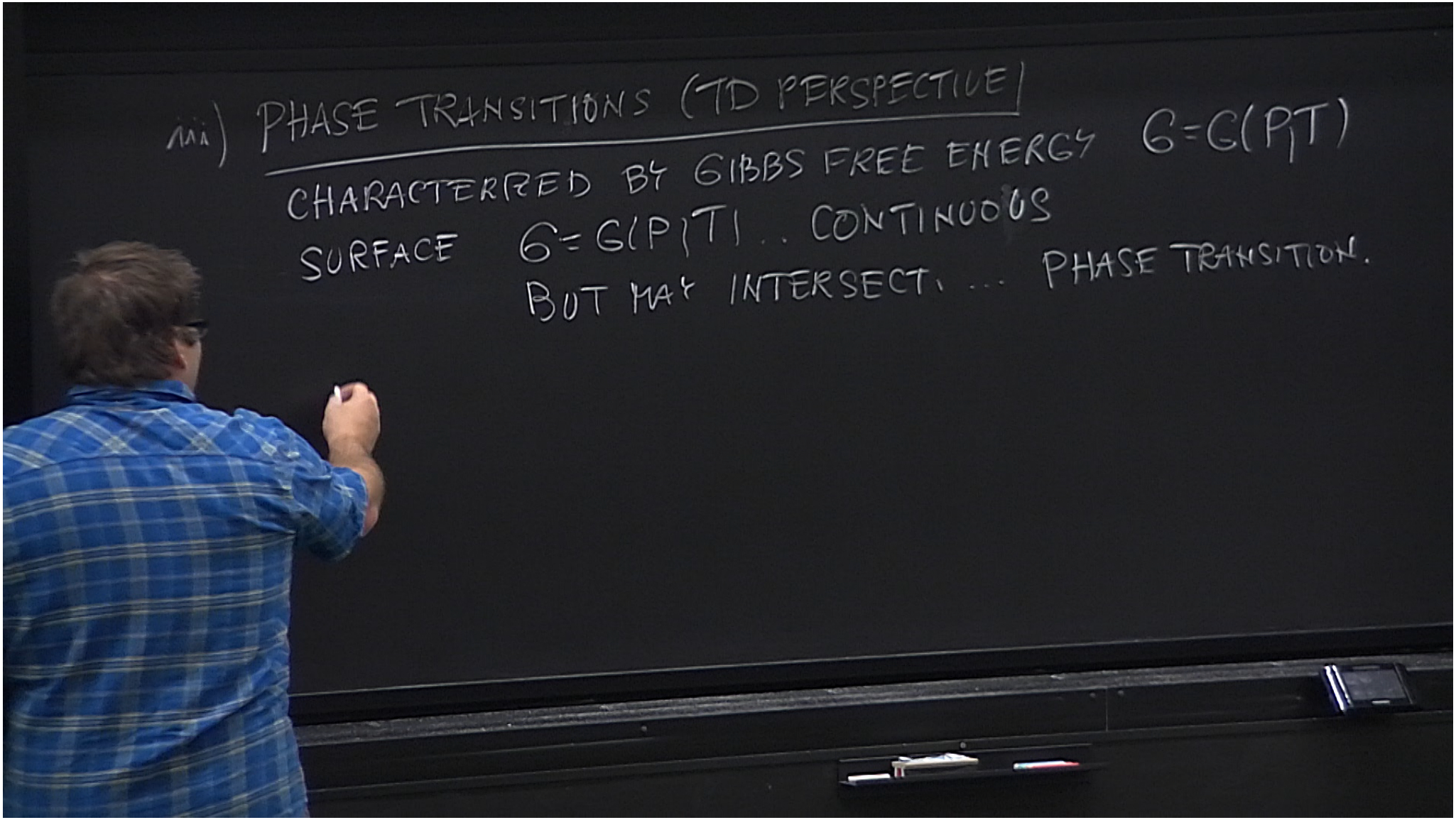
$(v-b)=T$

ASURES ATTRACTION
TWEEN PARTICLES.
CLUDED VOLUME
OF PARTICLES.

ISOTHERMS IN P-V DIAGRAM




ERMS IN P-V DIAGRAM
CRITICAL POINT
T ... HIGH
LIQUID
GAS
T=Tc
T<Tc
V
'S EQUAL AREA LAW
$P_{PT}(v_g - v_l) = \int_{v_l}^{v_g} P\,dv$
$\Leftrightarrow \boxed{\oint v\,dP = 0}$

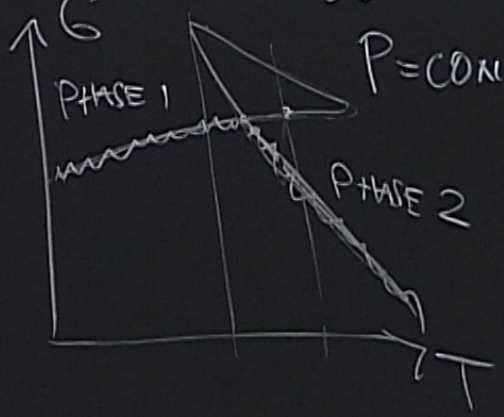

iii) PHASE TRANSITIONS (TD PERSPECTIVE)
CHARACTERISED BY GIBBS FREE ENERGY G=G(P,T)
SURFACE G=G(P,T) .. CONTINUOUS
BUT MAY INTERSECT, ... PHASE TRANSITION.

iii) PHASE TRANSITIONS (TD PERSPECTIVE)

CHARACTERIZED BY GIBBS FREE ENERGY $G = G(P,T)$

SURFACE $G = G(P,T)$ .. CONTINUOUS

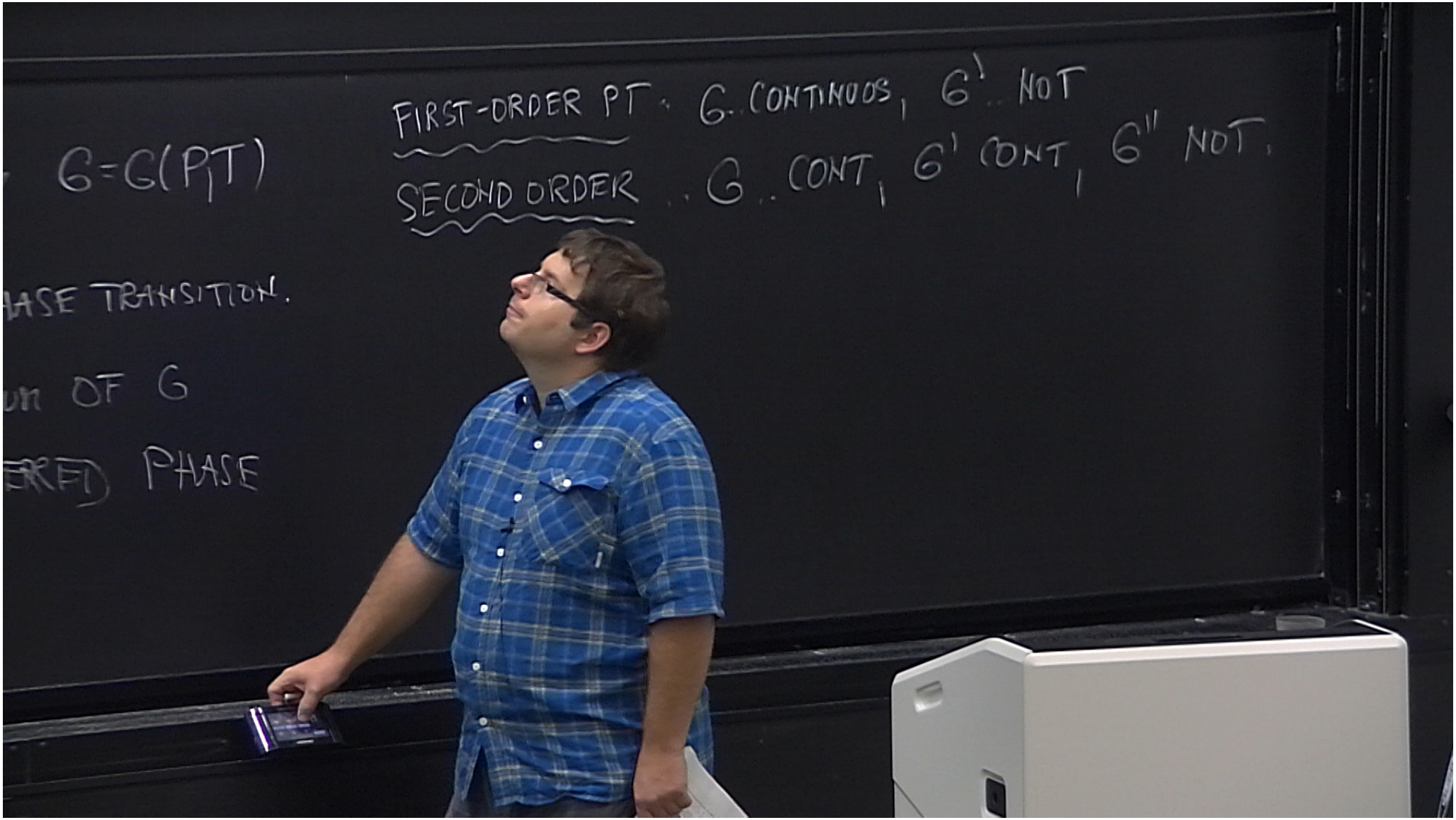
BUT MAY INTERSECT, ... PHASE TRANSITION.



P=CONST

GLOBAL MINIMUM OF G

≃ PREFERRED PHASE

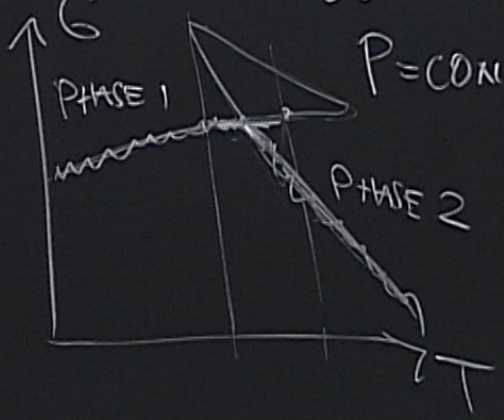

G=G(P,T)
FIRST-ORDER PT : G CONTINUOS, G' NOT
SECOND ORDER : G CONT, G' CONT, G'' NOT.
ASE TRANSITION.
ON OF G
ERED) PHASE

iii) PHASE TRANSITIONS

CHARACTERIZED BY GIBBS FREE ENERGY $G = G(P,T)$

SURFACE $G = G(P,T)$ .. CONTINUOUS

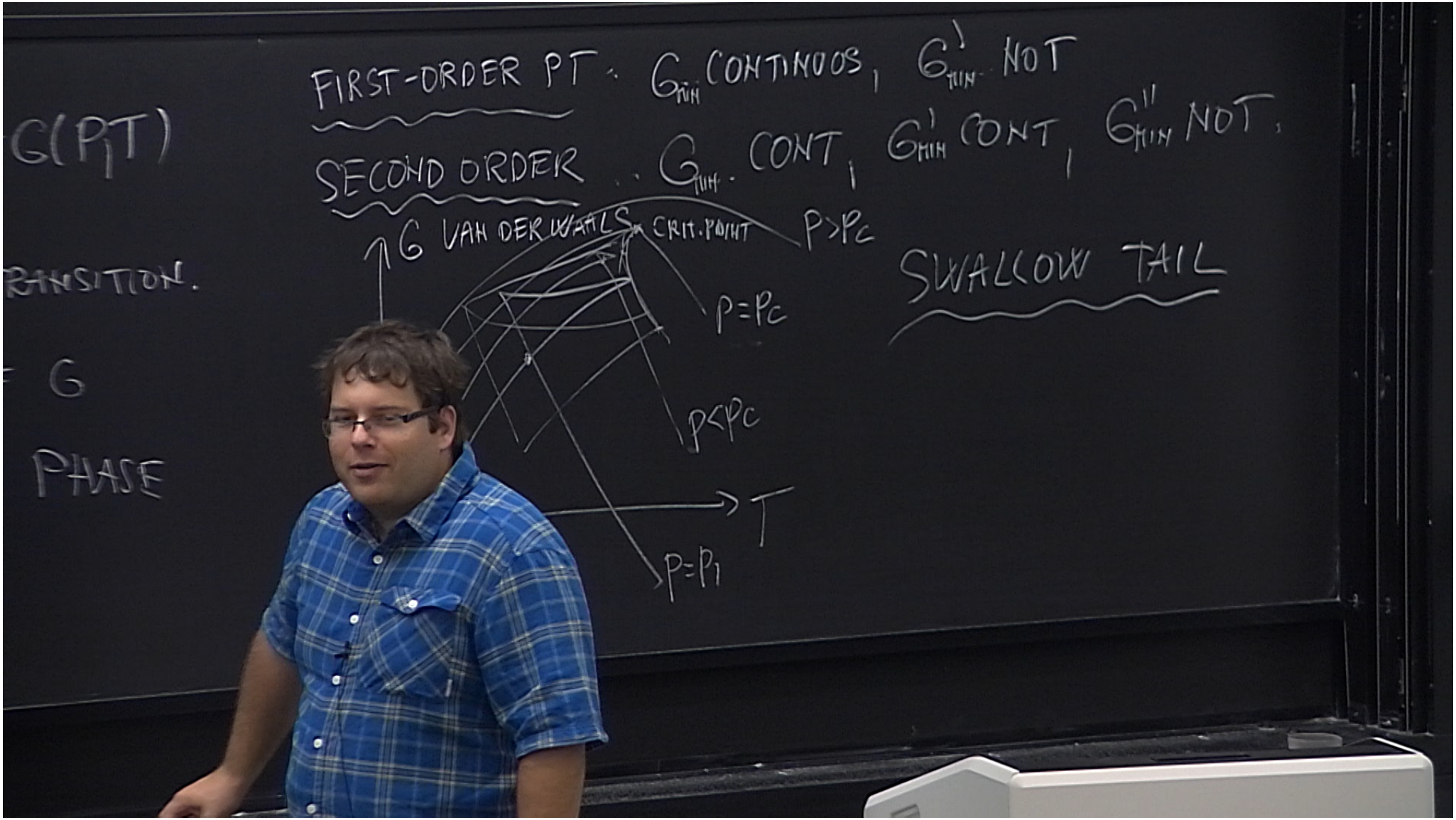
BUT MAY INTERSECT. ... PHASE TRANSITION.

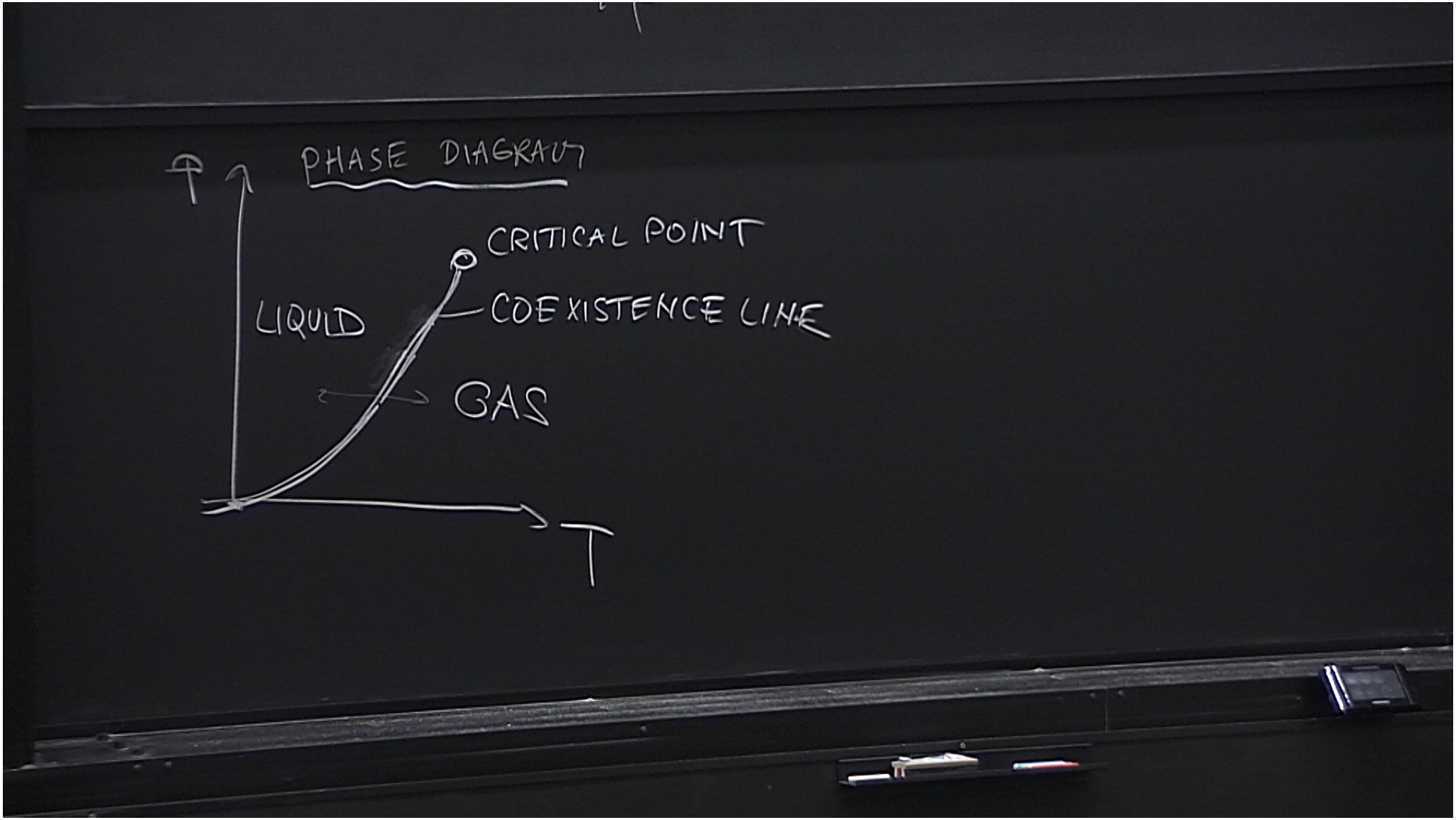


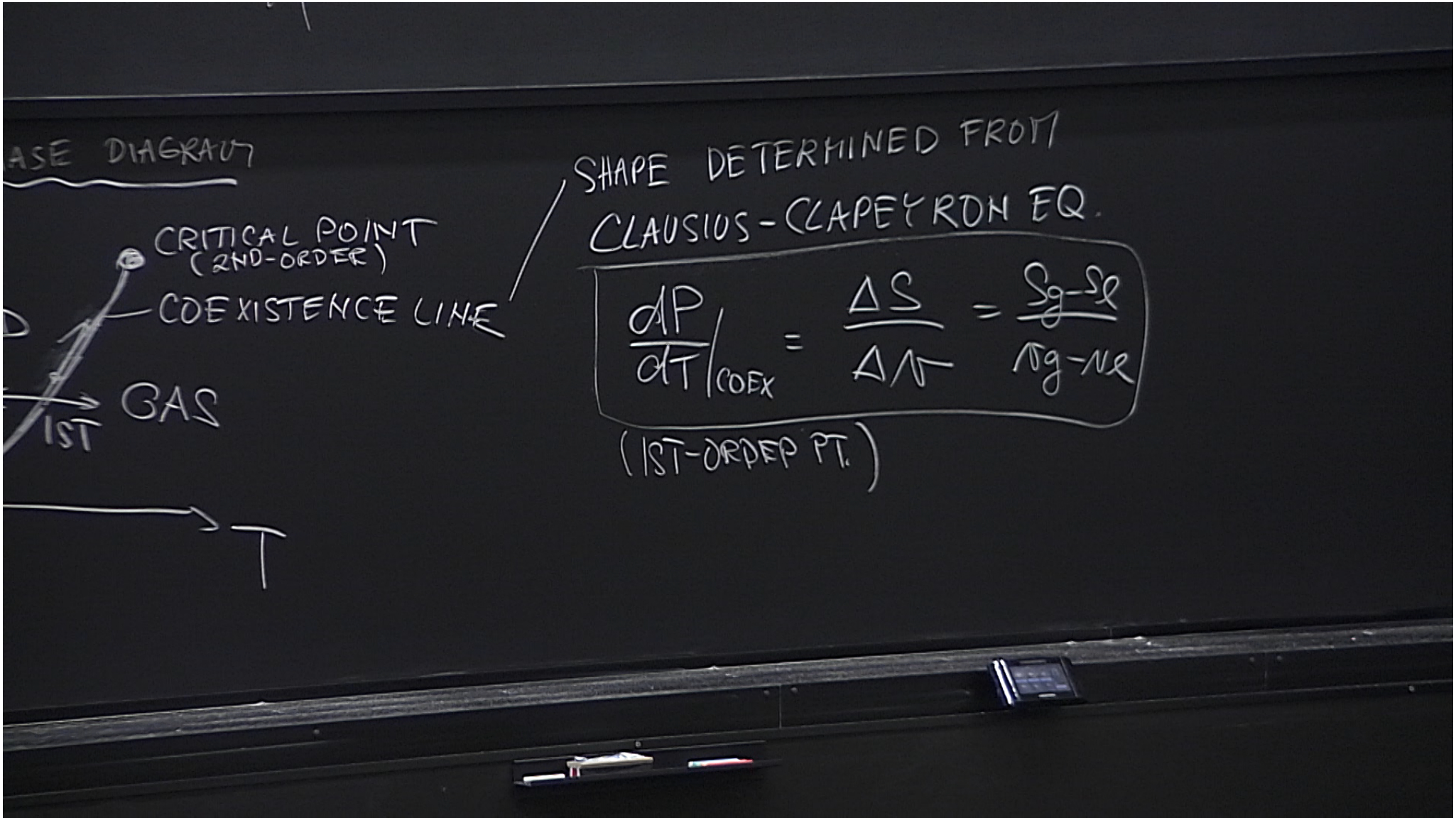
P = CONST

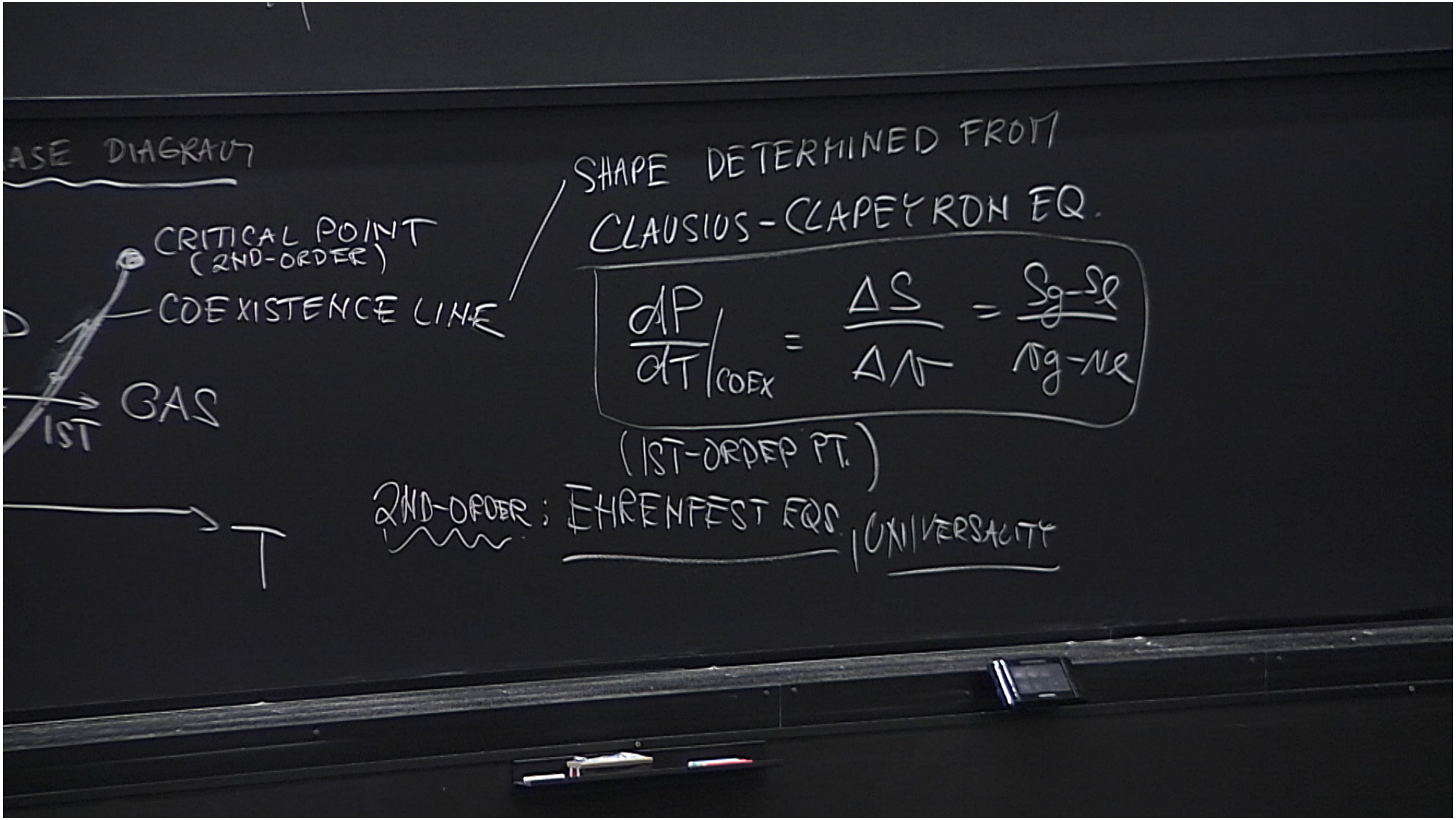
GLOBAL MINIMUM OF G

≃ PREFERRED PHASE


G(P,T)
TRANSITION.
= G
PHASE
FIRST-ORDER PT : G_{min} CONTINUOS, G'_{min} NOT
SECOND ORDER : G_{min} CONT, G'_{min} CONT, G''_{min} NOT.
G VAN DER WAALS
CRIT. POINT
P>Pc
P=Pc
P<Pc
P=P1
T
SWALLOW TAIL


PHASE DIAGRAM
CRITICAL POINT
COEXISTENCE LINE
LIQUID
GAS
T

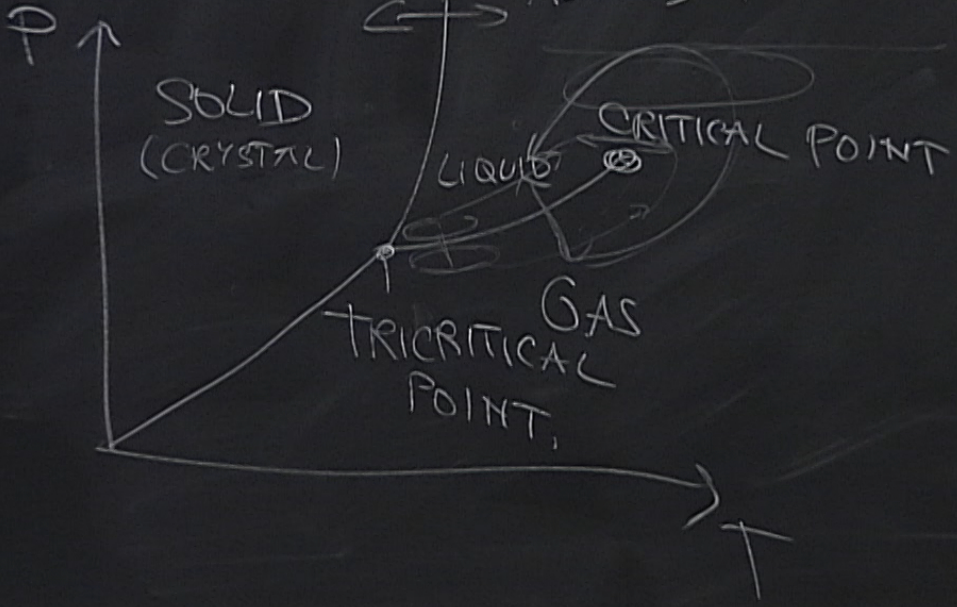

ASE DIAGRAM
CRITICAL POINT
(2ND-ORDER)
COEXISTENCE LINE
GAS
IST
T
SHAPE DETERMINED FROM
CLAUSIUS-CLAPEYRON EQ.
$\frac{dP}{dT}\Big|_{COEX} = \frac{\Delta S}{\Delta V} = \frac{S_g - S_\ell}{V_g - V_\ell}$
(IST-ORDER PT.)


ASE DIAGRAM
CRITICAL POINT
(2ND-ORDER)
COEXISTENCE LINE
GAS
1ST
T
SHAPE DETERMINED FROM
CLAUSIUS-CLAPEYRON EQ.
$\frac{dP}{dT}\Big|_{COEX} = \frac{\Delta S}{\Delta V} = \frac{S_g - S_\ell}{V_g - V_\ell}$
(1ST-ORDER PT.)
2ND-ORDER: EHRENFEST EQS. | UNIVERSALITY

HER EXAMPLES OF PHASE TRANSITIONS

SOLID-LIQUID-GAS

ALWAYS PT.



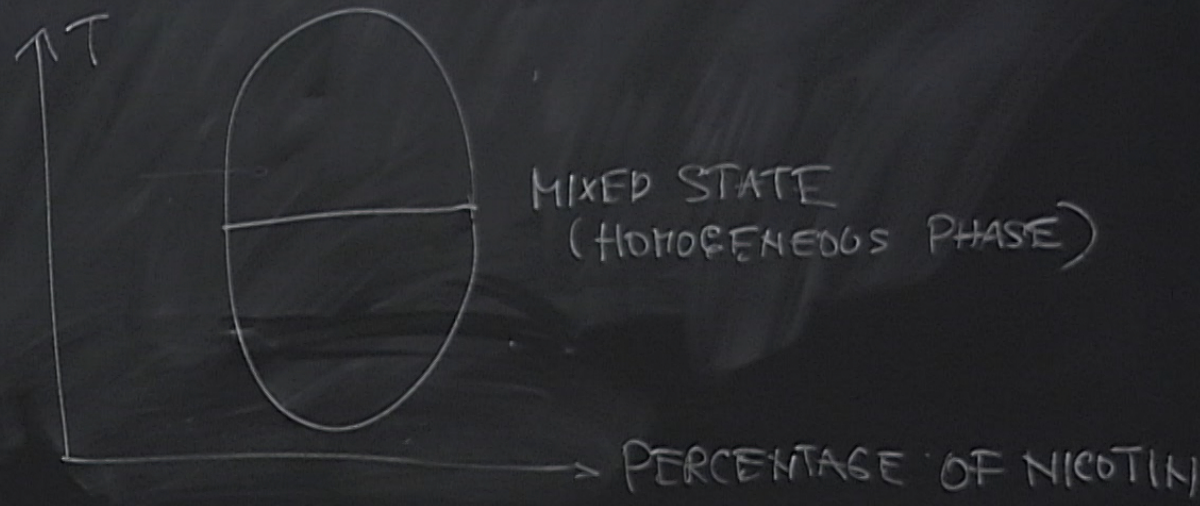
- REENTRANT PT. ≡ IF

ENTRANT PT. ≡ IF A MONOTONIC VARIATION OF ONE TD VARIABLE RESULTS IN SEVERAL PHASE TRANSITIONS SUCH THAT THE FINAL STATE IS MACROSCOPICALLY SIMILAR TO INITIAL ONE.

RESULTS IN

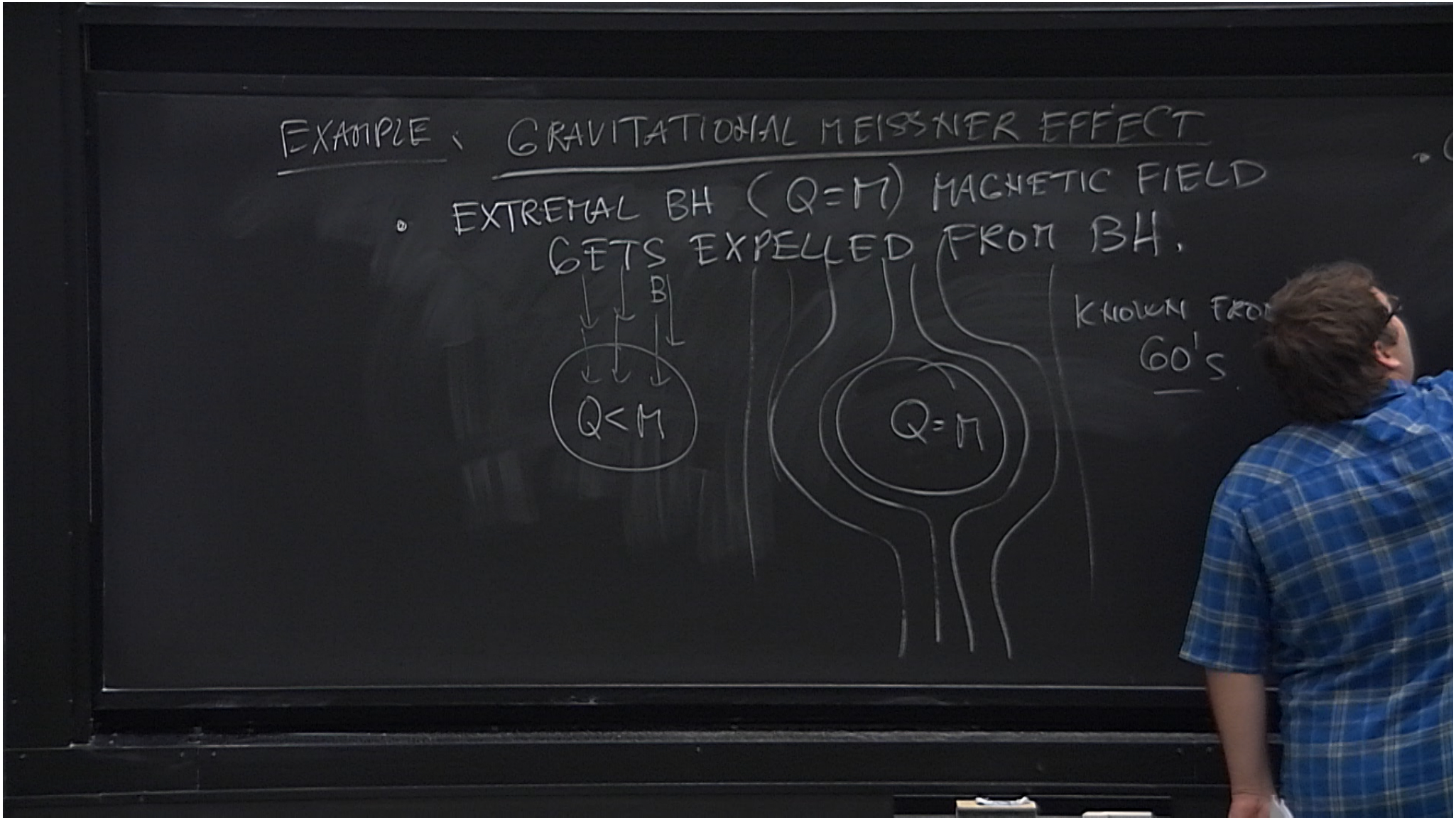
THE FINAL STATE IS MACROSCOPICALLY SIMILAR TO

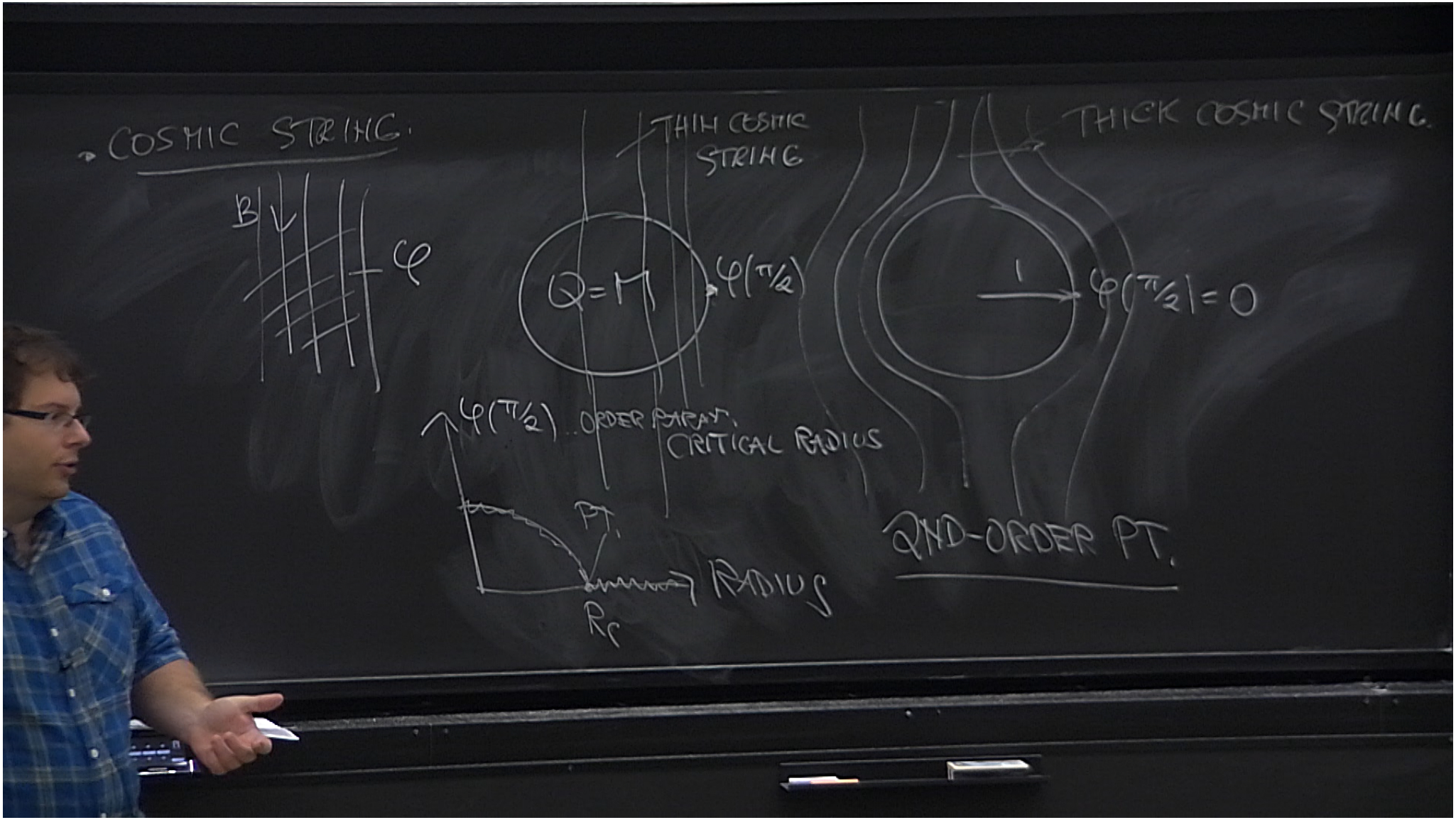
(1904 HUDSON)



$$\frac{\partial T}{\partial V} = -\frac{\partial (U - TS)}{\partial V} = T\frac{\partial S}{\partial V}$$

ORIGIN OF PRESSURE IS ENTROPIC.


EXAMPLE: GRAVITATIONAL MEISSNER EFFECT
• EXTREMAL BH (Q=M) MAGNETIC FIELD GETS EXPELLED FROM BH.
B
Q<M
Q=M
KNOWN FRO
60's


COSMIC STRING.
B
φ
THIN COSMIC STRING
Q=M
φ(π/2)
THICK COSMIC STRING.
1
φ(π/2)=0
φ(π/2) ORDER PARAM.
CRITICAL RADIUS
PT.
RADIUS
Rc
2ND-ORDER PT.