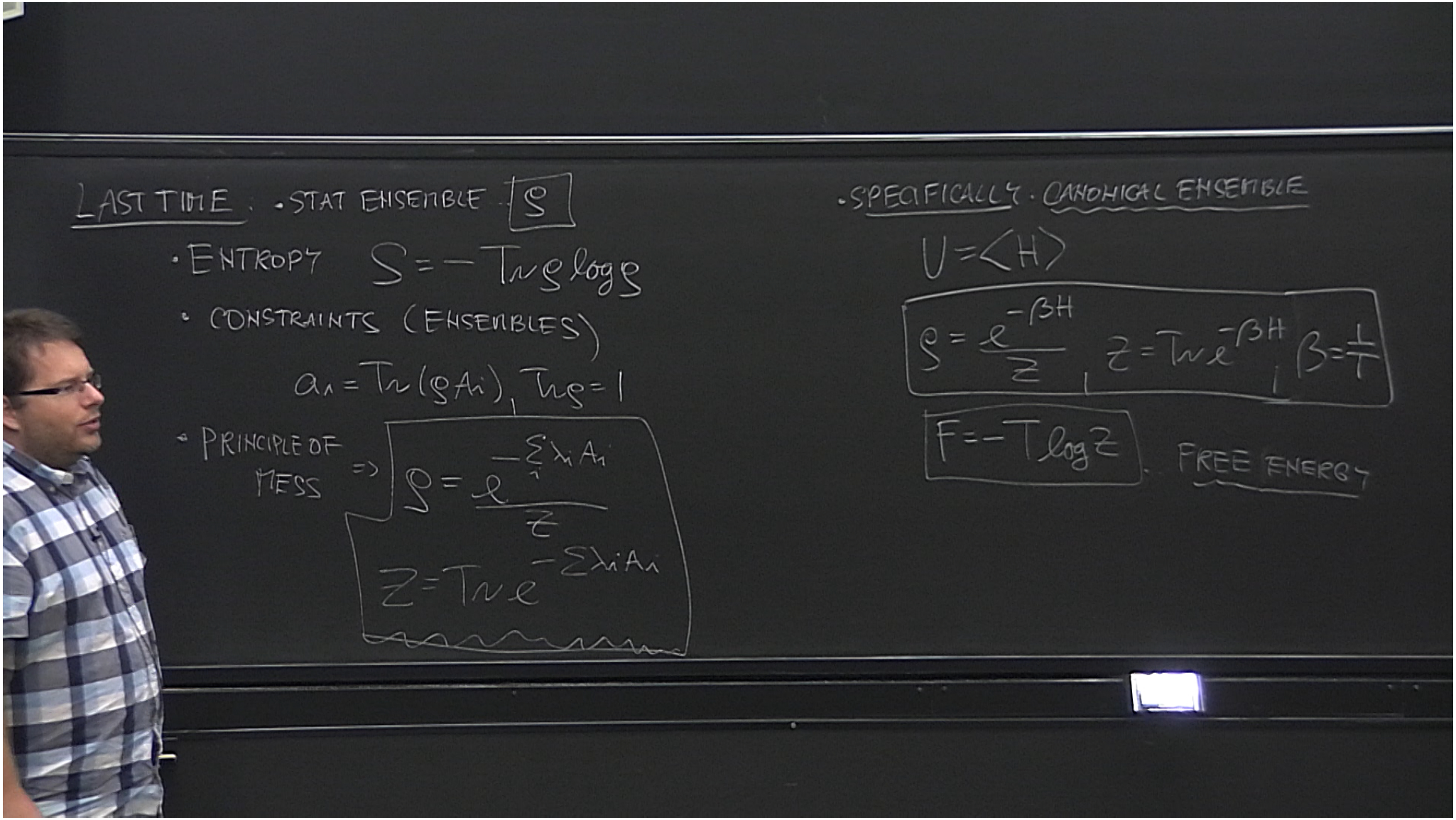
Title: PSI 2019/2020 - Statistical Physics - Lecture 2

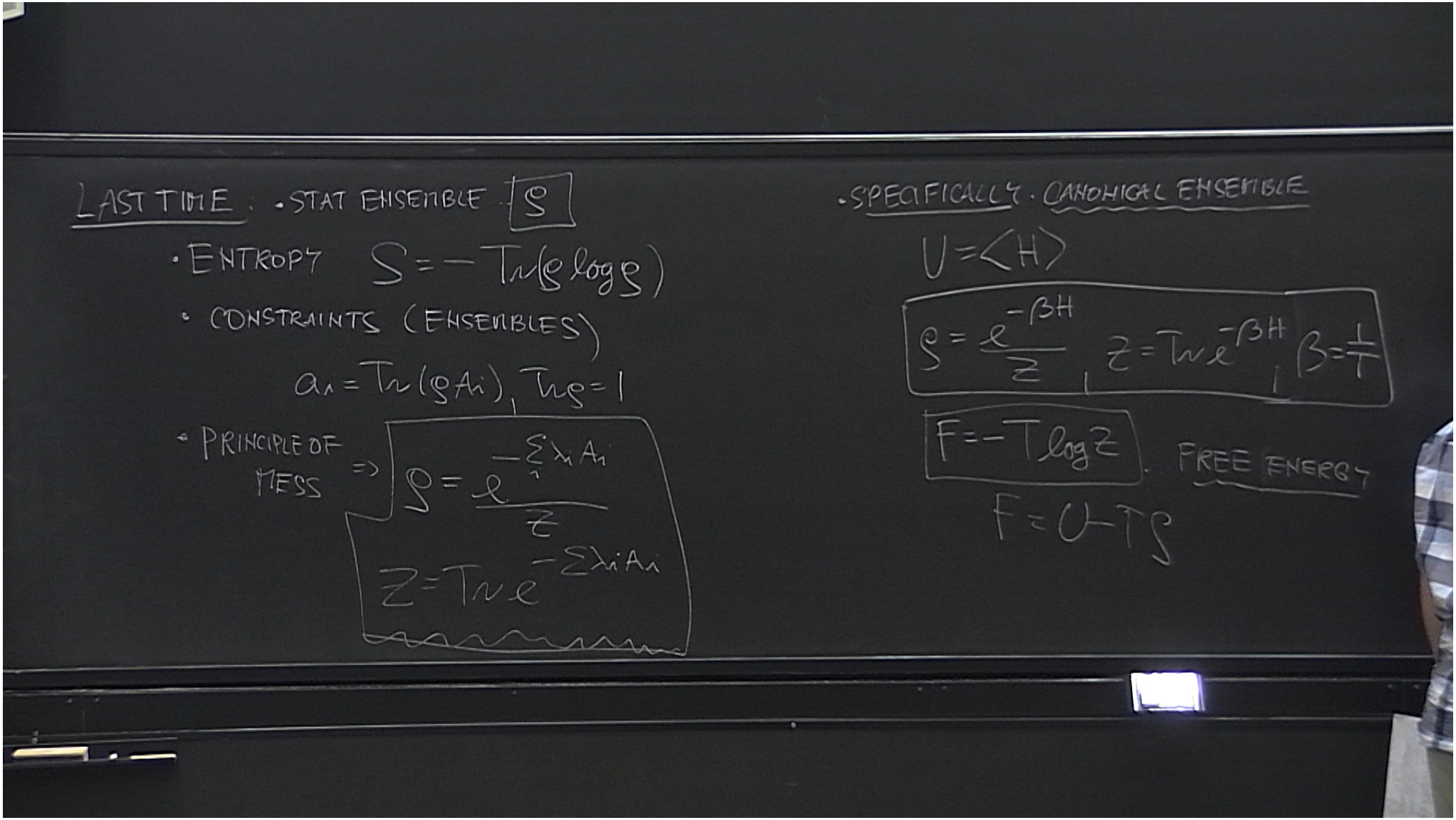
Speakers: David Kubiznak

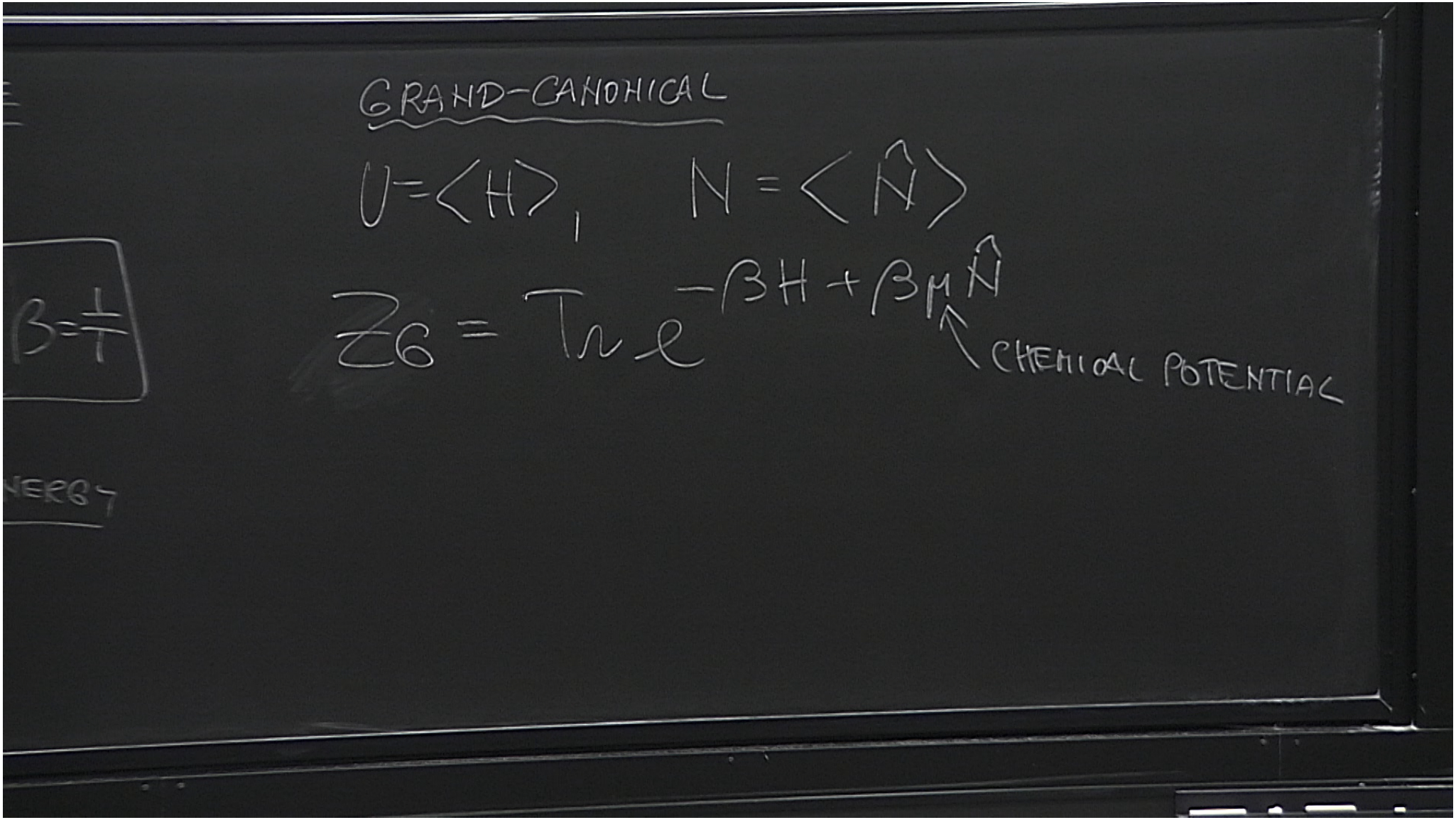
Collection: PSI 2019/2020 - Statistical Physics (Kubiznak)

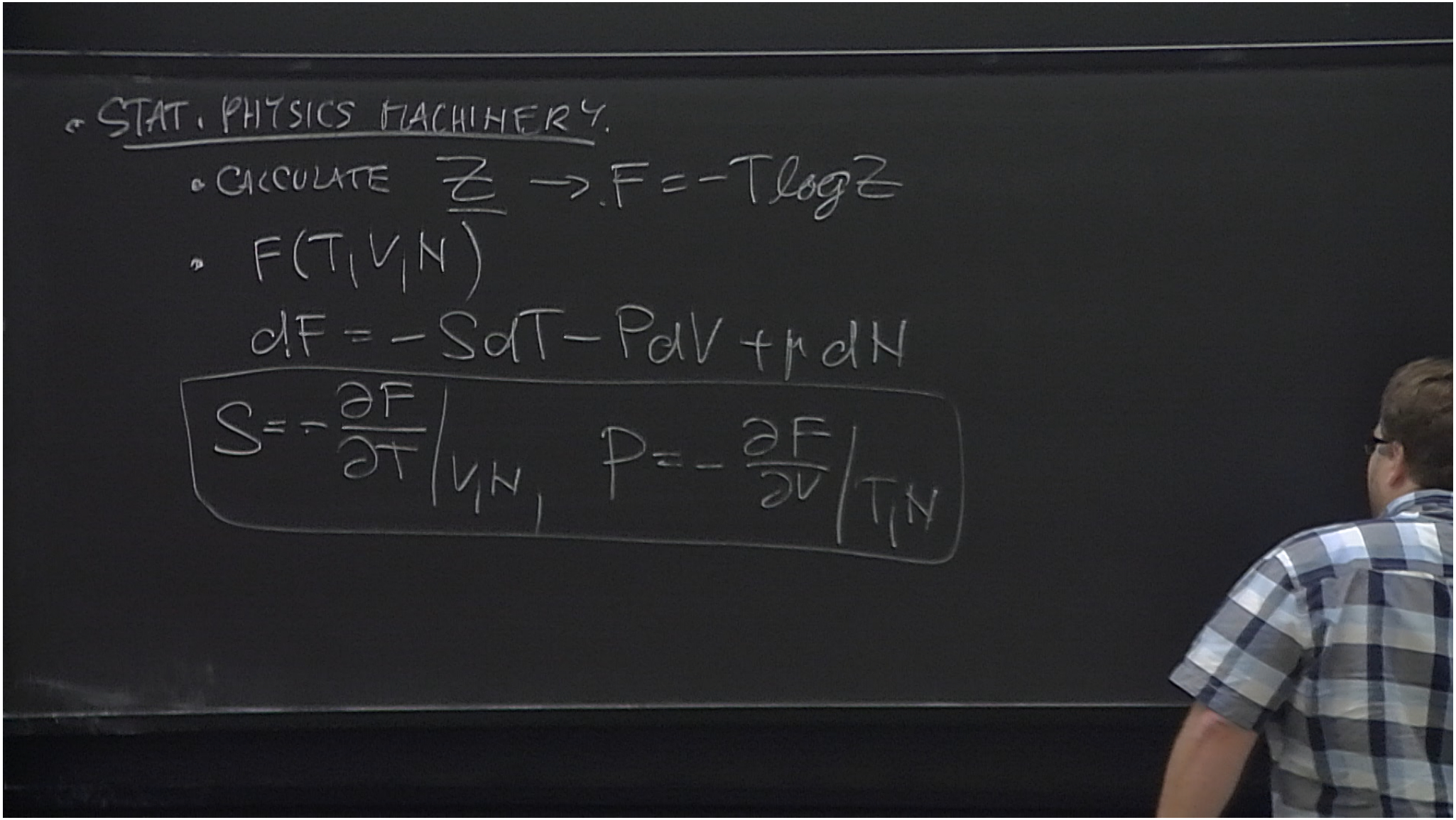
Date: August 26, 2019 - 2:00 PM

URL: http://pirsa.org/19080074


LAST TIME: • STAT ENSEMBLE: ρ
• ENTROPY $S = -\mathrm{Tr}\,\rho\log\rho$
• CONSTRAINTS (ENSEMBLES)
$a_i = \mathrm{Tr}(\rho A_i)$, $\mathrm{Tr}\,\rho = 1$
• PRINCIPLE OF MESS =>
$\rho = \frac{e^{-\sum \lambda_i A_i}}{Z}$
$Z = \mathrm{Tr}\, e^{-\sum \lambda_i A_i}$
• SPECIFICALLY: CANONICAL ENSEMBLE
$U = \langle H \rangle$
$\rho = \frac{e^{-\beta H}}{Z}$, $Z = \mathrm{Tr}\, e^{-\beta H}$, $\beta = \frac{1}{T}$
$F = -T\log Z$ FREE ENERGY


LAST TIME: • STAT ENSEMBLE: ρ
• ENTROPY $S = -\mathrm{Tr}(\rho \log \rho)$
• CONSTRAINTS (ENSEMBLES)
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• PRINCIPLE OF MESS $\Rightarrow$
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• SPECIFICALLY · CANONICAL ENSEMBLE
$U = \langle H \rangle$
$\rho = \frac{e^{-\beta H}}{Z}$, $Z = \mathrm{Tr}\, e^{-\beta H}$, $\beta = \frac{1}{T}$
$F = -T \log Z$ · FREE ENERGY
$F = U - TS$


GRAND-CANONICAL
$U = \langle H \rangle$, $N = \langle \hat{N} \rangle$
$Z_G = Tr\, e^{-\beta H + \beta\mu \hat{N}}$
CHEMICAL POTENTIAL
$\beta = \frac{1}{T}$


STAT. PHYSICS MACHINERY.
CALCULATE Z → F = −T log Z
F(T, V, N)
dF = −S dT − P dV + μ dN
S = −(∂F/∂T)|V,N , P = −(∂F/∂V)|T,N

• EX: IDEAL GAS (CLASSICAL)

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$$

• EX: IDEAL GAS (CLASSICAL)

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$$ .. NON-INTERACTING PARTICLES

$$Z = \# \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N d\vec{p}_1 \cdots d\vec{p}_N \, e^{-\beta H}$$

$$= \# V^N \left[\int d\vec{p}_1 \, e^{-\beta \frac{\vec{p}_1^{\,2}}{2m}} \right]^N$$

$$\left(\sqrt{\frac{2\pi m}{\beta}} \right)^3$$

• EX: IDEAL GAS (CLASSICAL)

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$$ .. NON-INTERACTING PARTICLES

$$\cdot\ Z = \# \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N d\vec{p}_1 \cdots d\vec{p}_N\ e^{-\beta H}$$

$$= \# V^N \left[\int d\vec{p}_1\ e^{-\beta \frac{\vec{p}_1^{\,2}}{2m}} \right]^N = \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}N} V^N$$

$$\left(\sqrt{\frac{2\pi m}{\beta}}^{\,3} \right)$$

$$F = -T \log Z = -\frac{3}{2} N T \log(2\pi m T) - N T \log V$$

$$F = -T \log Z = -\frac{3}{2} NT \log(2\pi m T) - NT \log V$$

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

$$F = -T \log Z = -\frac{3}{2} NT \log(2\pi m T) - NT \log V$$

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

$$\boxed{P v = T, \quad v = \frac{V}{N}}$$

IDEAL GAS LAW

$$F = -T \log Z = -\frac{3}{2} N T \log(2\pi m T) - N T \log V$$

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IDEAL GAS LAW

EQUATION OF STATE

$$F = -T \log Z = -\frac{3}{2} NT \log(2\pi m T) - NT \log V$$

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

$$\boxed{P v = T, \quad v = \frac{V}{N}}$$

IDEAL GAS LAW

EQUATION OF STATE

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = \frac{3}{2} N \log(2\pi m T) + N \log V + \frac{3}{2} N$$

- $U = F + TS = \frac{3}{2} NT$ .. EQUIPARTITION THEOREM
- $U(T, \cancel{V})$ .. CHARACTERISTIC OF AN IDEAL GAS

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial (\cancel{U} - TS)}{\partial V}\Big|_{T,N}$$ .. PRESSURE COMES FROM S RATHER THAN U.

- $U = F + TS = \frac{3}{2} NT$ .. EQUIPARTITION THEOREM
- $U(T, \cancel{V})$ .. CHARACTERISTIC OF AN IDEAL GAS.

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial (\cancel{U} - TS)}{\partial V}\Big|_{T,N}$$

↑ ENTROPIC ORIGIN OF PRESSURE

.. PRESSURE COMES FROM S RATHER THAN U.

$$C_V = \frac{\delta Q}{\delta T}\Big|_V = T \frac{\partial S}{\partial T}\Big|_V = \frac{3}{2} N$$

$$C_P = T \frac{\partial S}{\partial T}\Big|_P$$

- $U = F + TS = \frac{3}{2} NT$ .. EQUIPARTITION THEOREM
- $U(T, \cancel{V})$ .. CHARACTERISTIC OF AN IDEAL GAS

$$P = -\frac{\partial F}{\partial V} = -\frac{\partial (\cancel{U} - TS)}{\partial V}\Big|_{T,N}$$

↑ ENTROPIC ORIGIN OF PRESSURE

PRESSURE COMES FROM S RATHER THAN U.

$$C_V = \frac{\delta Q}{\delta T}\Big|_V = T \frac{\partial S}{\partial T}\Big|_V = \frac{3}{2} N$$

$$C_P = T \frac{\partial S}{\partial T}\Big|_P \overset{\text{DO IT}}{=} \frac{5}{2} N$$

MYER'S LAW

$$\gamma = \frac{C_P}{C_V} = \frac{5}{3}$$

- TRUE GASES ARE INTERACTING → CORRECTIONS TO IDEAL GAS LAW.

$$P = nT\left(1 + nB_2 + n^2 B_3 + n^3 B_4 \ldots\right)$$

INCLUDING MORE TERMS NEED NOT TO GIVE A BETTER ANSWER

- INSTEAD CONSIDER VAH DER WAALS EQUATION (1873)

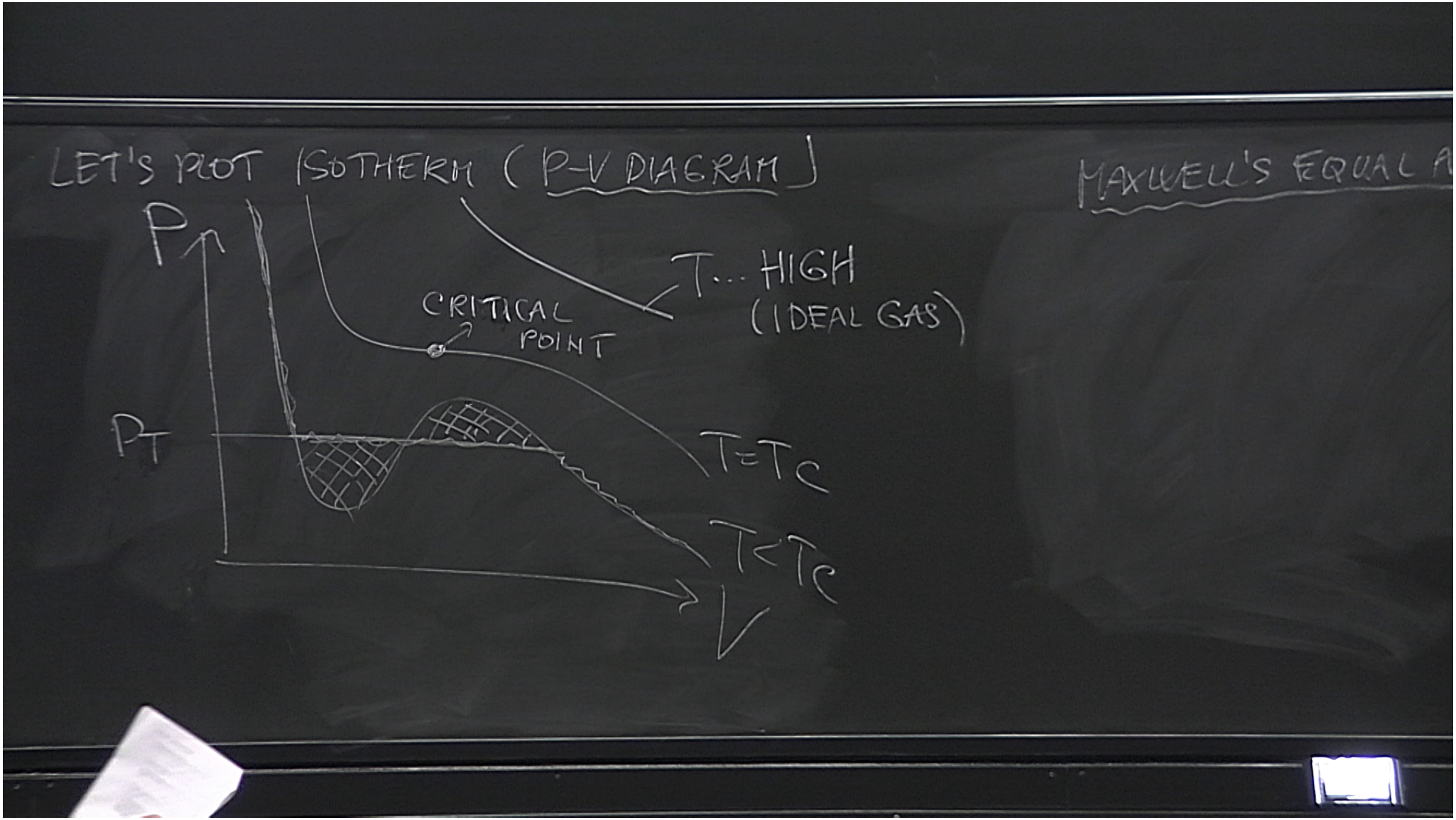
$$\left(P + \frac{a}{v^2}\right)(v - b) = T$$

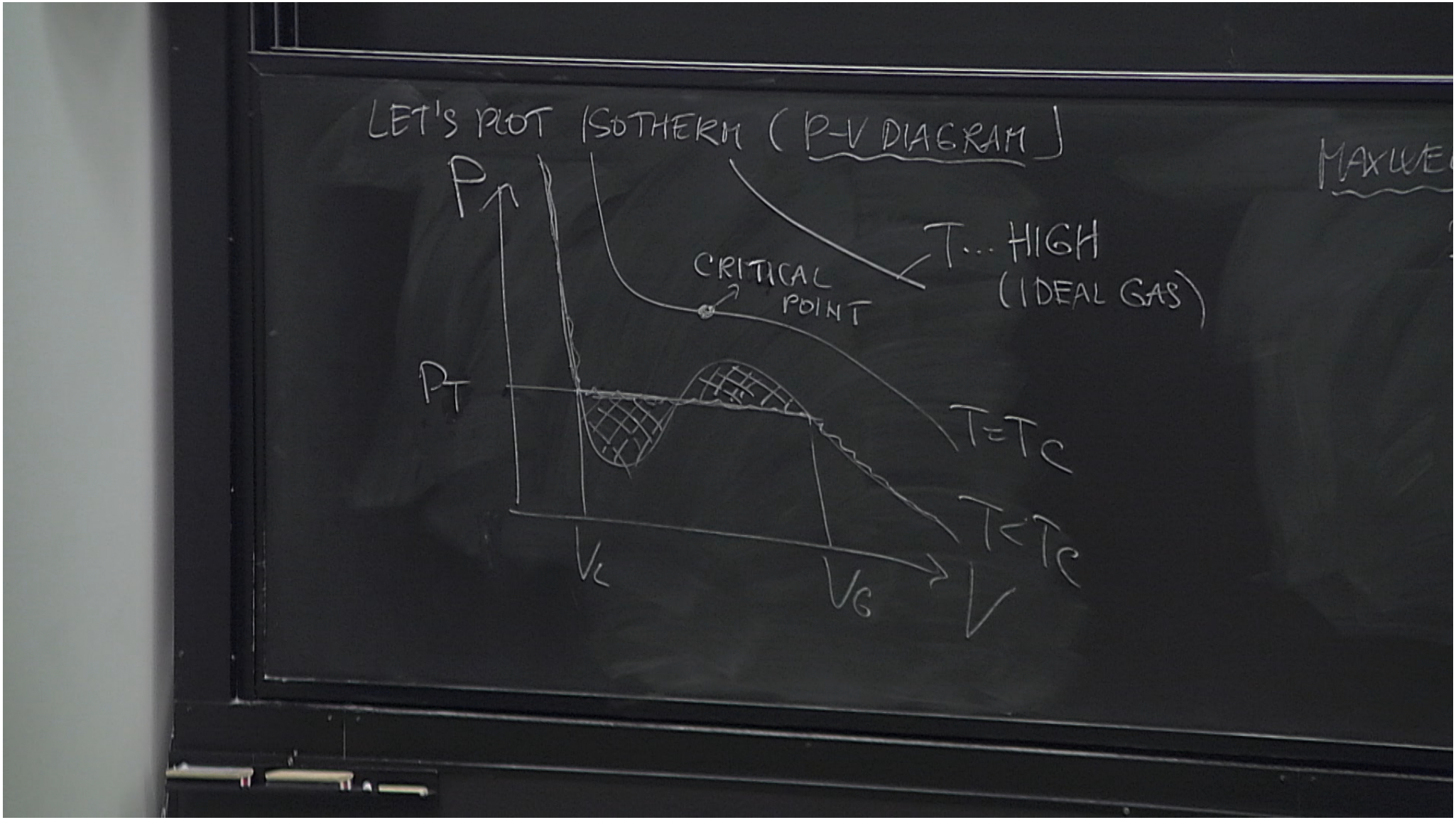
NP... 1910

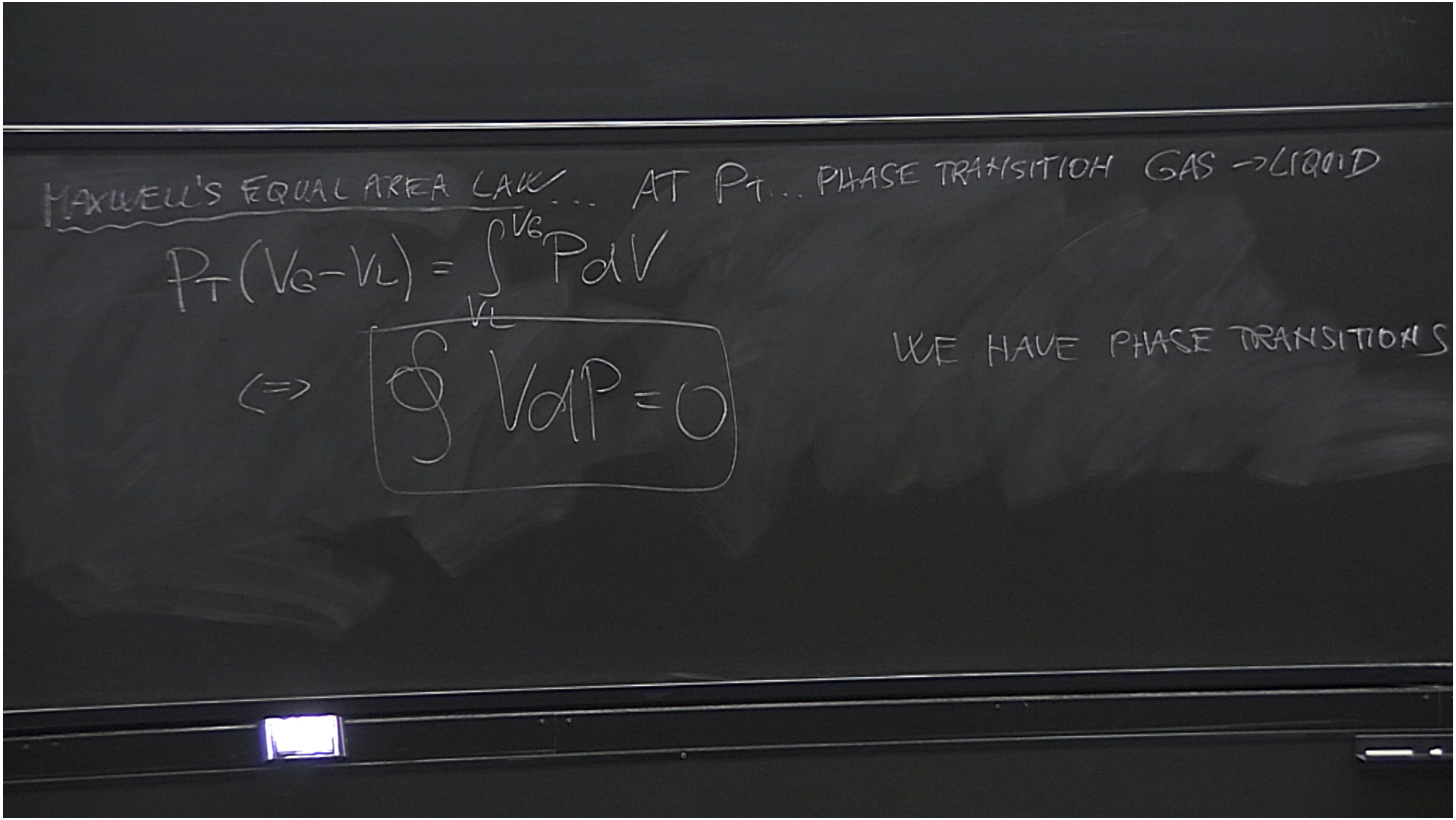
WORKS EXTREMELY WELL FOR ALMOST ALL GASES (UPON WE MEASURE a, b)

$a > 0$ ... INTERACTION

b VOLUME OF PARTICLES


LET'S PLOT ISOTHERM (P-V DIAGRAM)
MAXWELL'S EQUAL A
P
T... HIGH
(IDEAL GAS)
CRITICAL
POINT
PT
T=Tc
T<Tc
V


LET'S PLOT ISOTHERM (P-V DIAGRAM)
P
T... HIGH
(IDEAL GAS)
CRITICAL
POINT
P_T
T=Tc
T<Tc
V_L
V_G
V


MAXWELL'S EQUAL AREA LAW... AT P_T... PHASE TRANSITION GAS -> LIQUID
$P_T(V_G - V_L) = \int_{V_L}^{V_G} P\,dV$
$\Leftrightarrow$ $\oint V\,dP = 0$
WE HAVE PHASE TRANSITIONS

$$P = nT\left(1 + nB_2 + n^2 B_3 + n^3 B_4 \ldots\right)$$

- PHASE TRANSITIONS

TO UNDERSTAND PTS FROM TD POINT OF VIEW
WE LOOK AT GIBBS FREE ENERGY

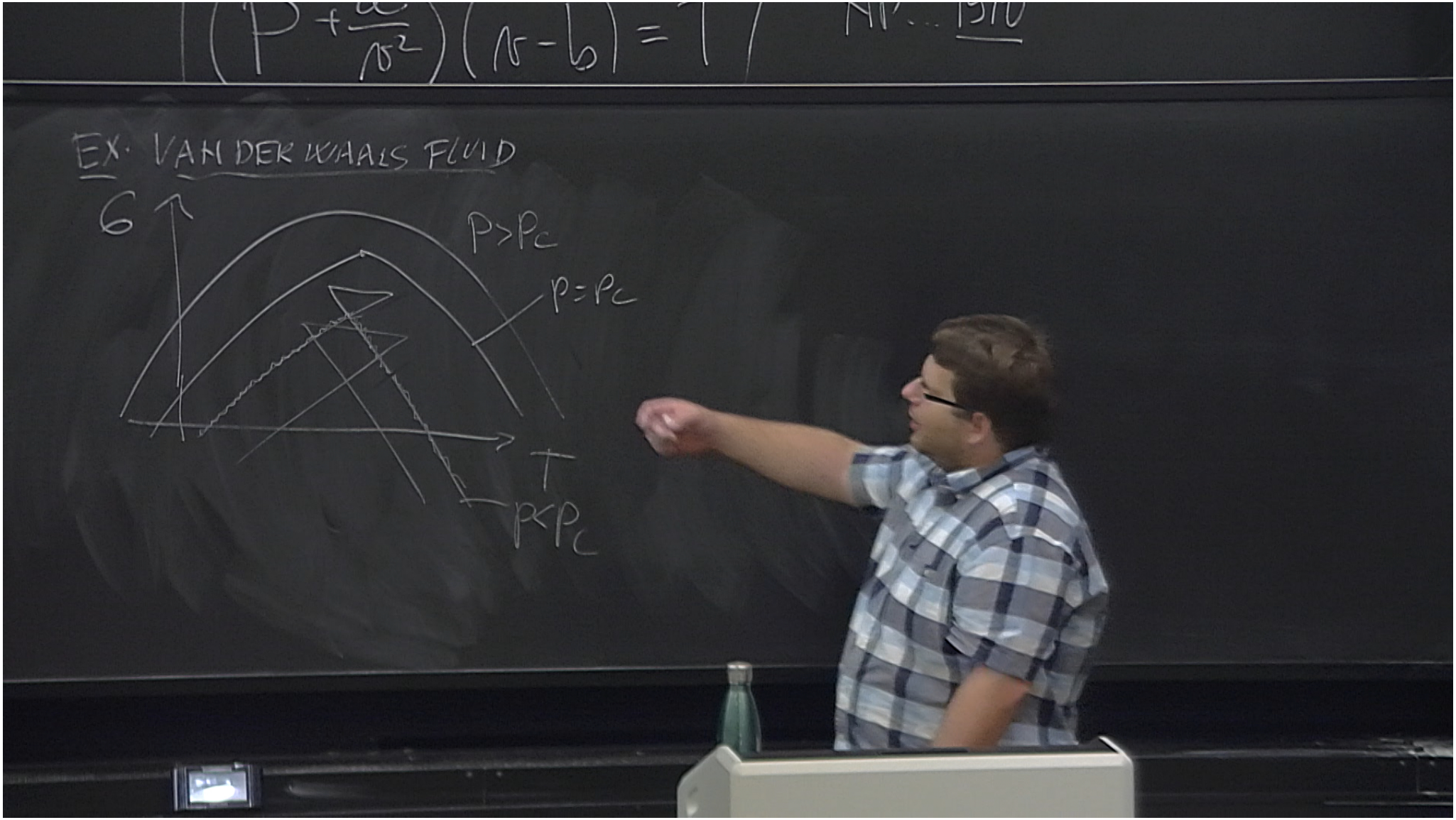
$$G(T, P)$$

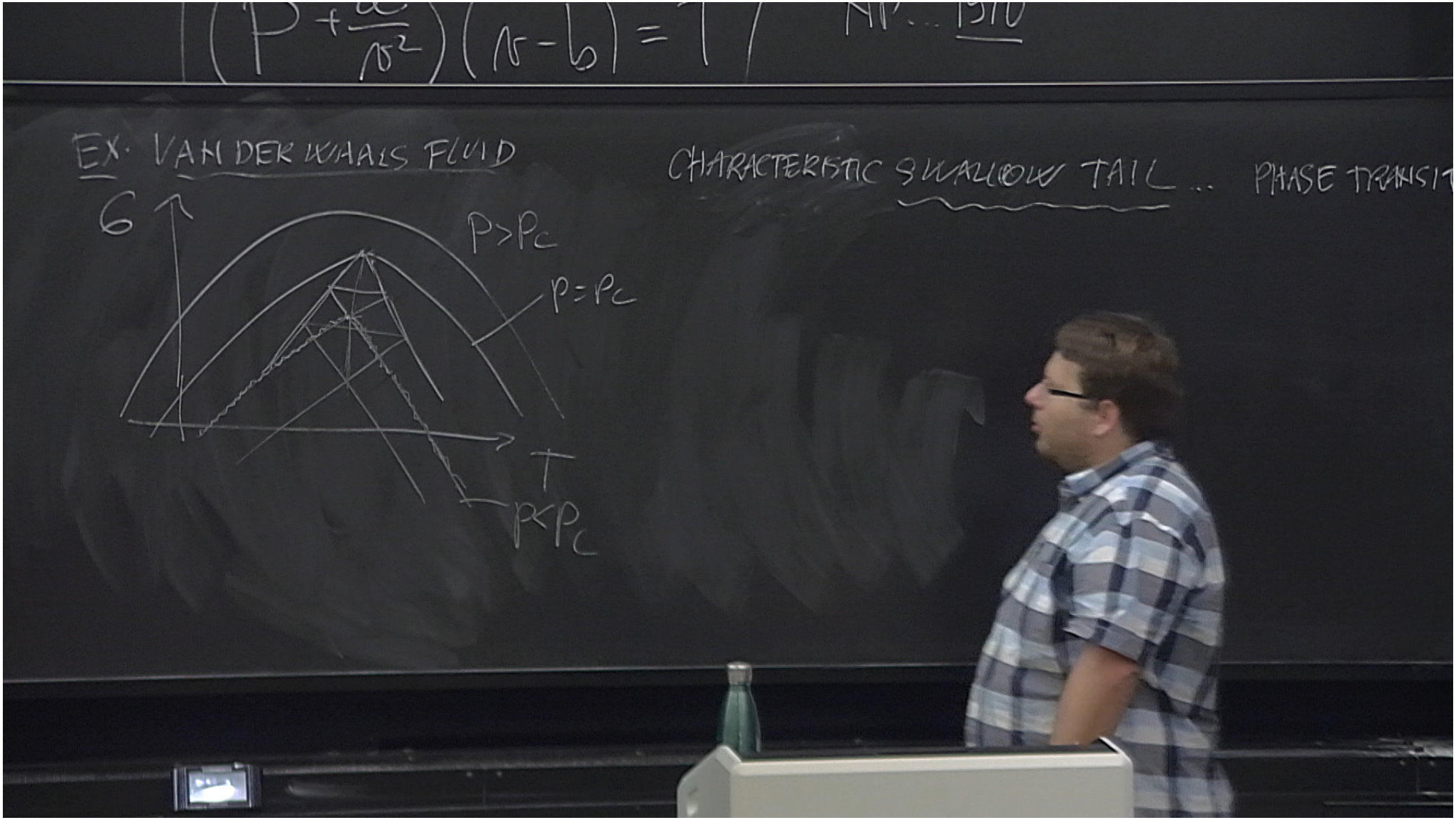
↑ GLOBAL MINIMUM ≃ STABLE EQ PHASE

IF NON-ANALYTICITIES ⇒ PHASE TRANSITIONS.

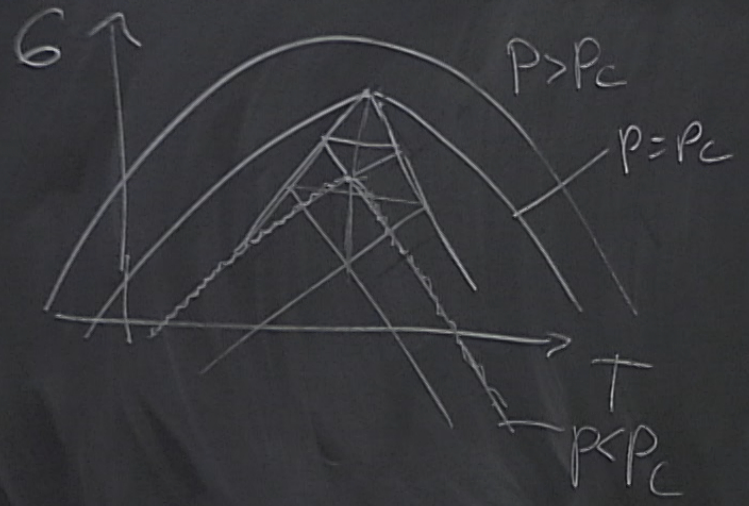
EX. V




EX. VAN DER WAALS FLUID
G
P>Pc
P=Pc
T
P<Pc

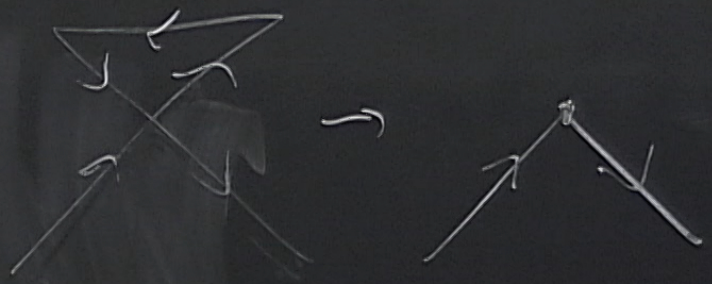

$\left(P + \frac{a}{v^2}\right)(v - b) = T$
EX. VAN DER WAALS FLUID
G
P>Pc
P=Pc
T
P<Pc
CHARACTERISTIC SWALLOW TAIL ..

EX. VAN DER WAALS FLUID



CHARACTERISTIC SWALLOW TAIL ... PHASE TRANSI

FOLLOWIN THE GLOBAL MINIMUM (AT GIVEN P)



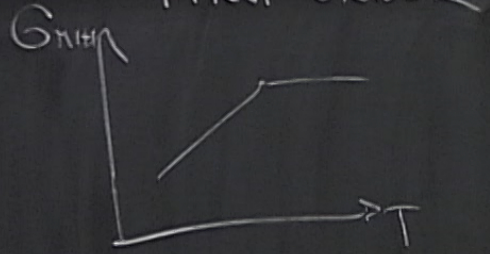
GLOBAL MINIMUM ⇔ STABLE EQ PHASE

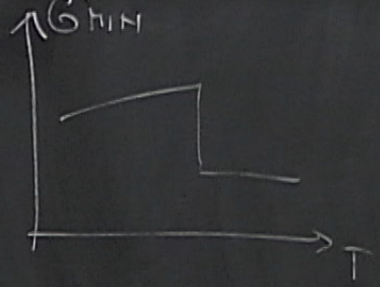
IF NON-ANALECITIES ⇒ PHASE TRANSITIONS.



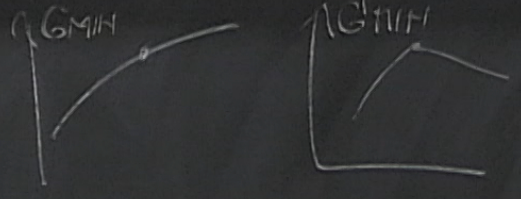
CLASSIFICATION OF PT

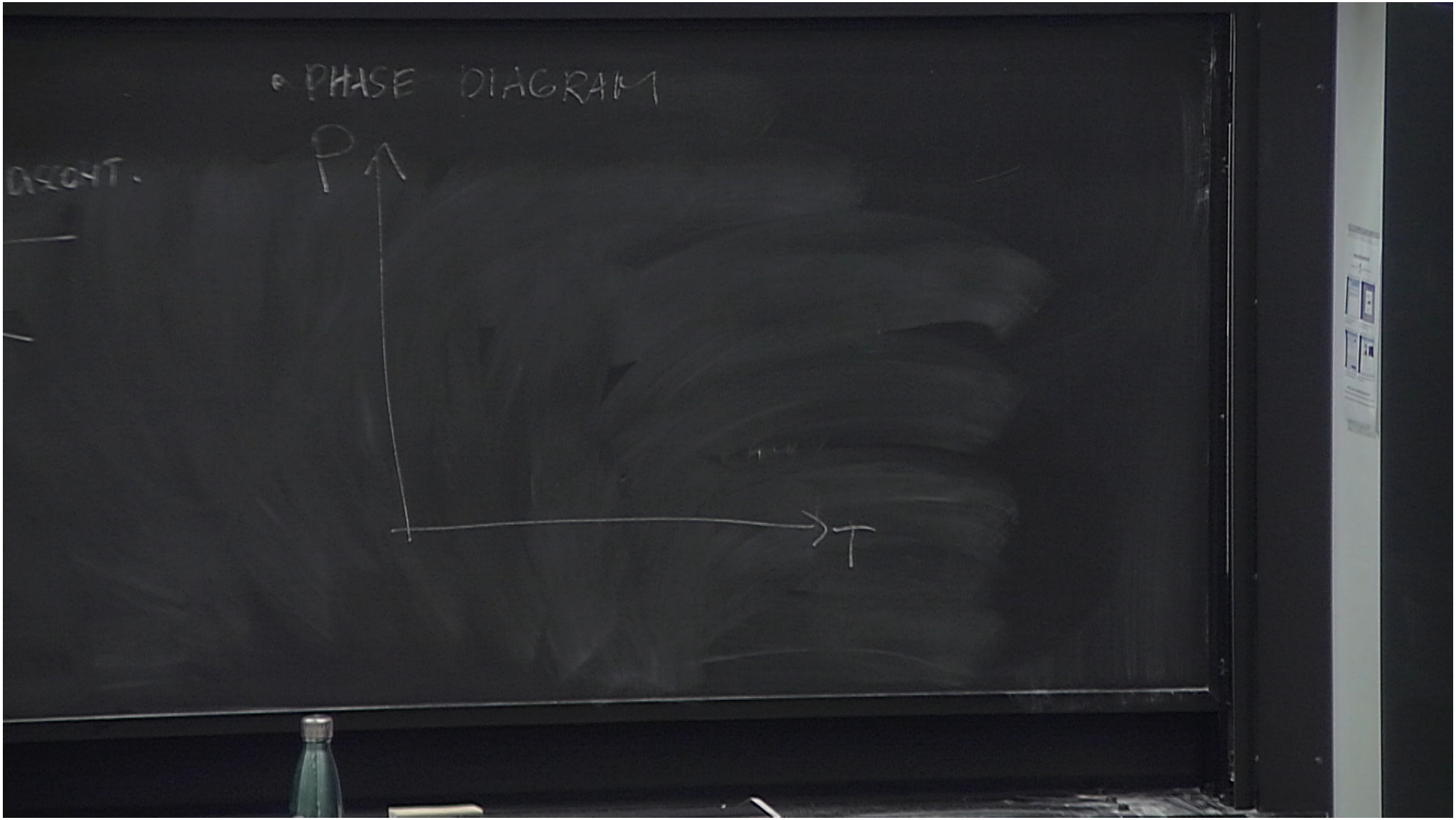
FIRST ORDER

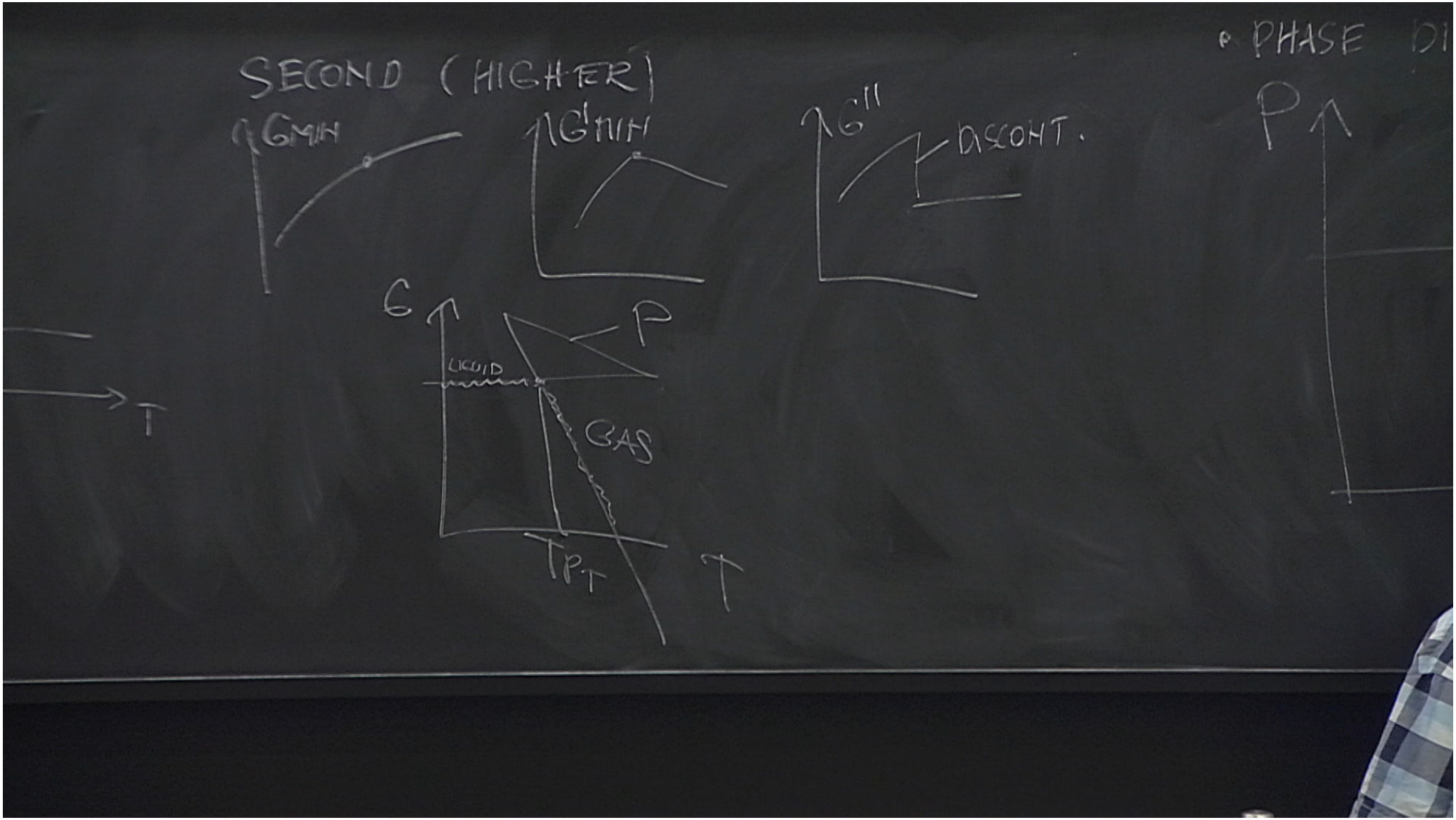


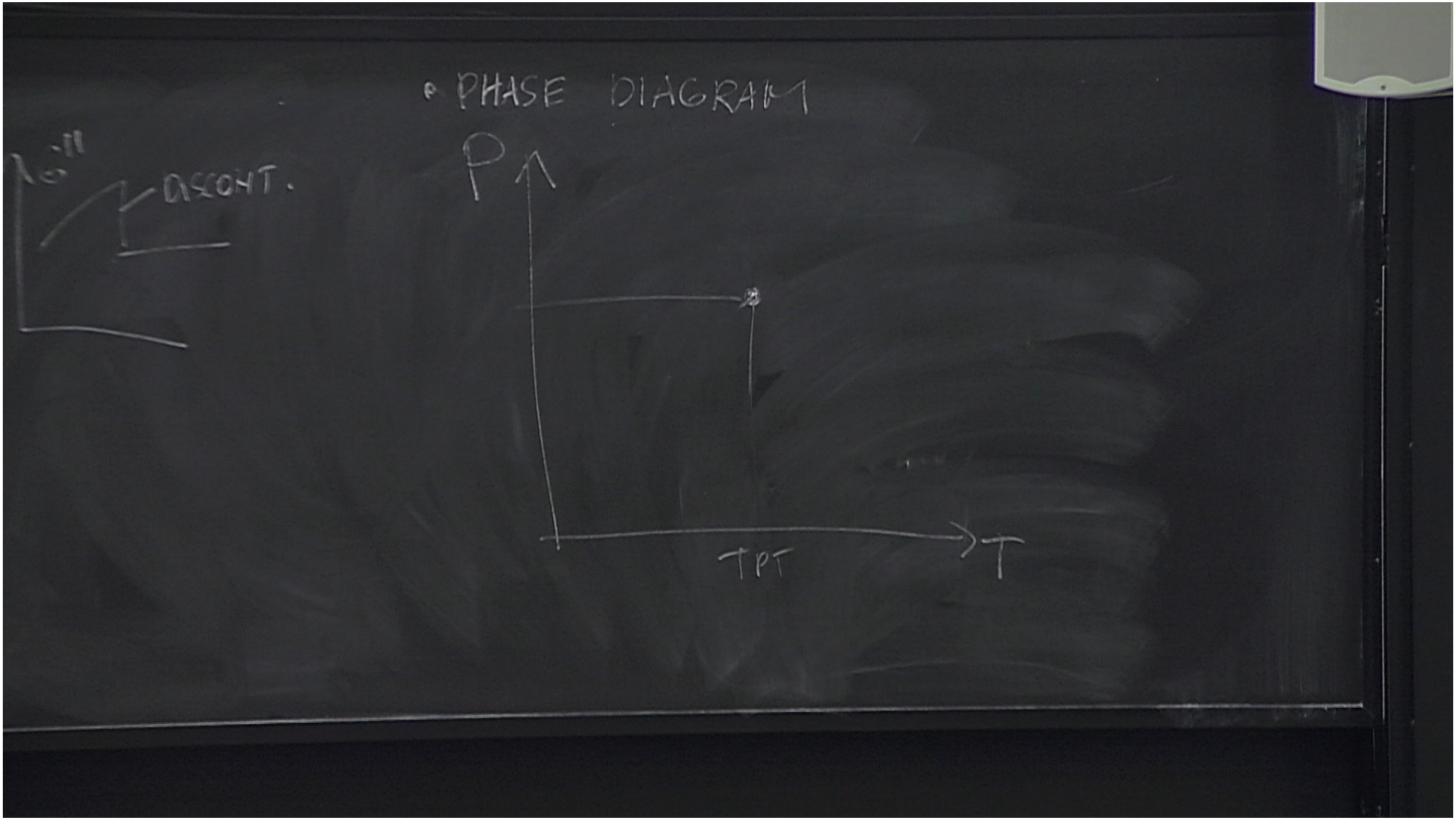


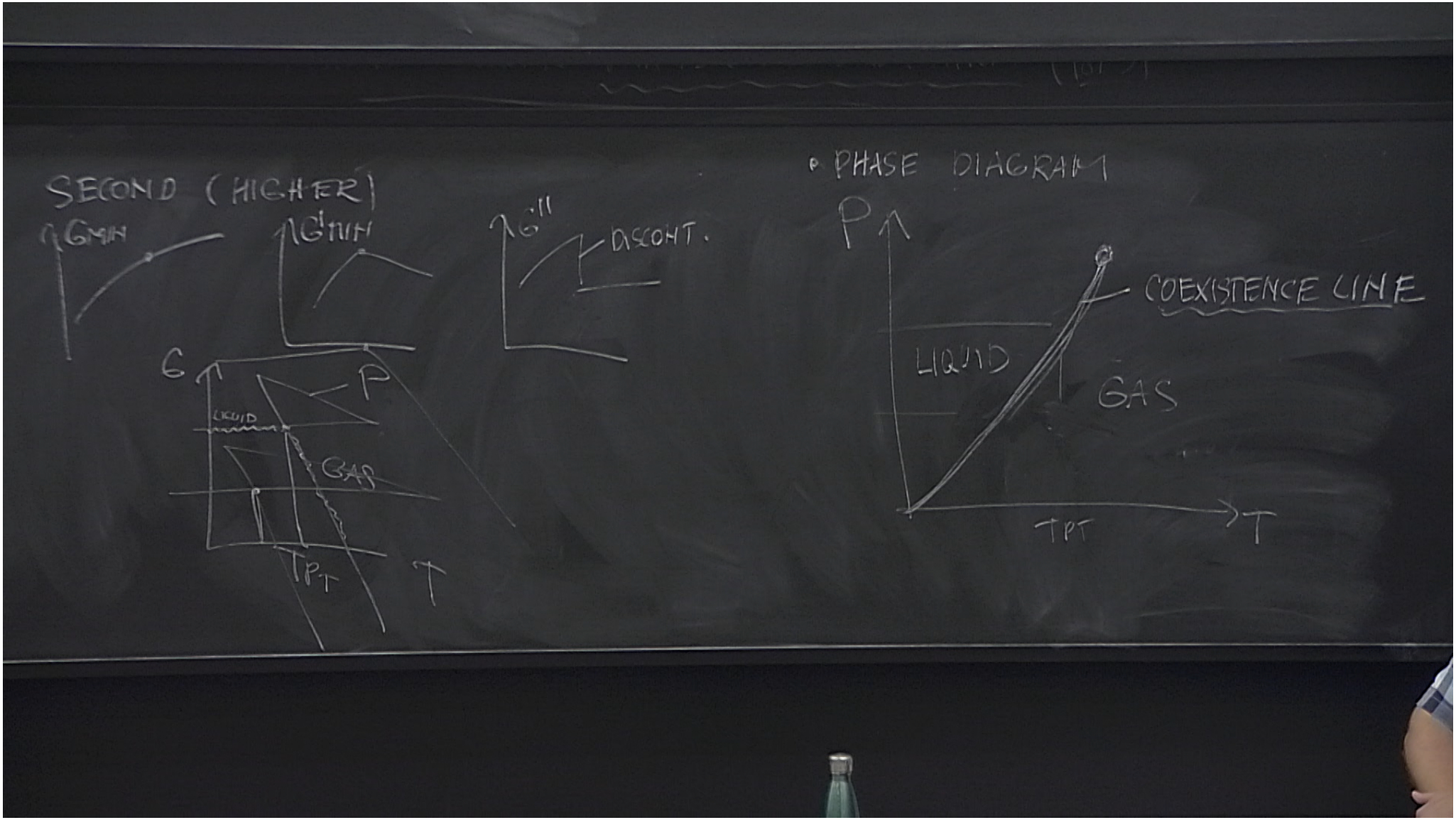
SECOND (HIGHER)

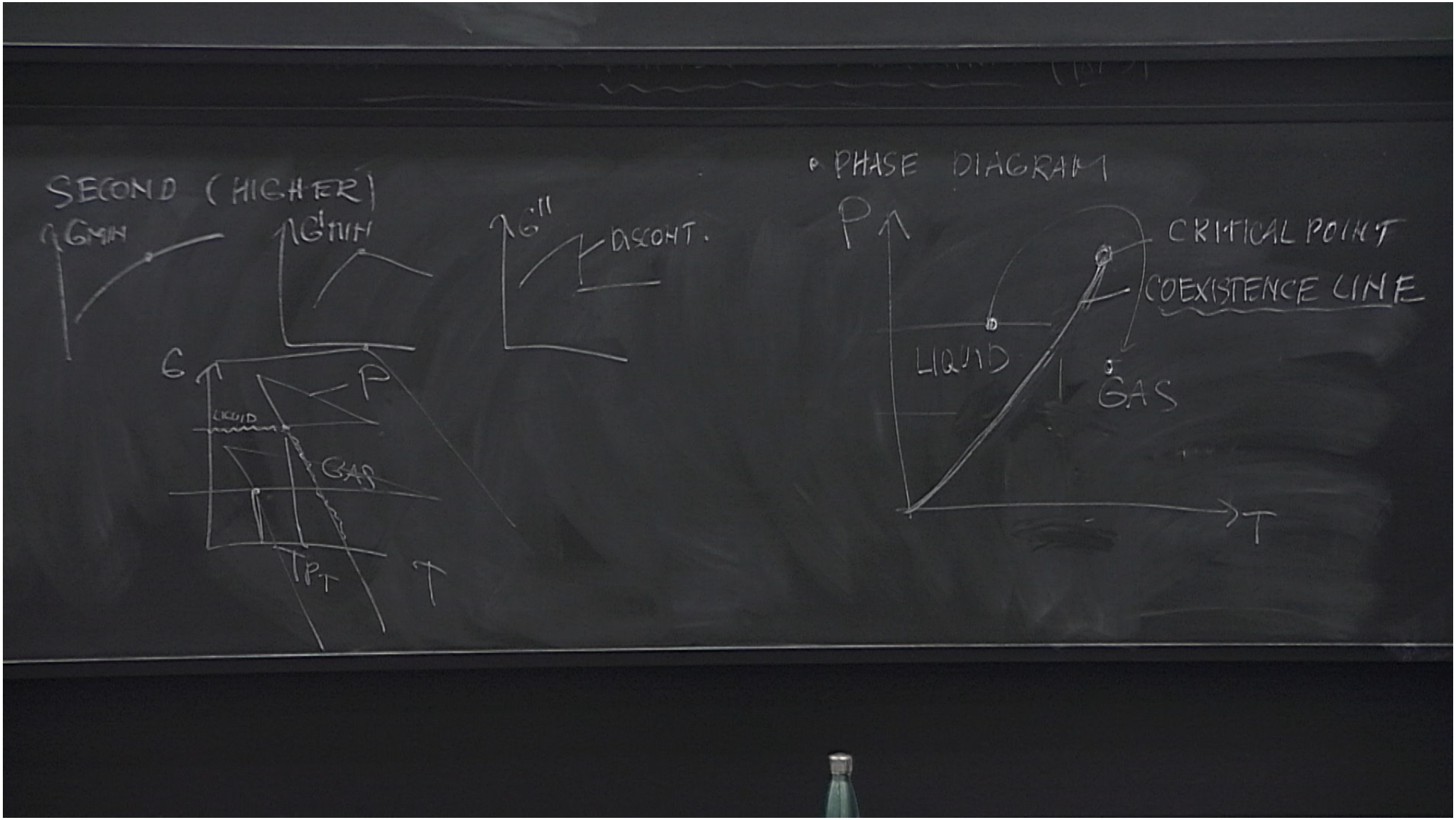


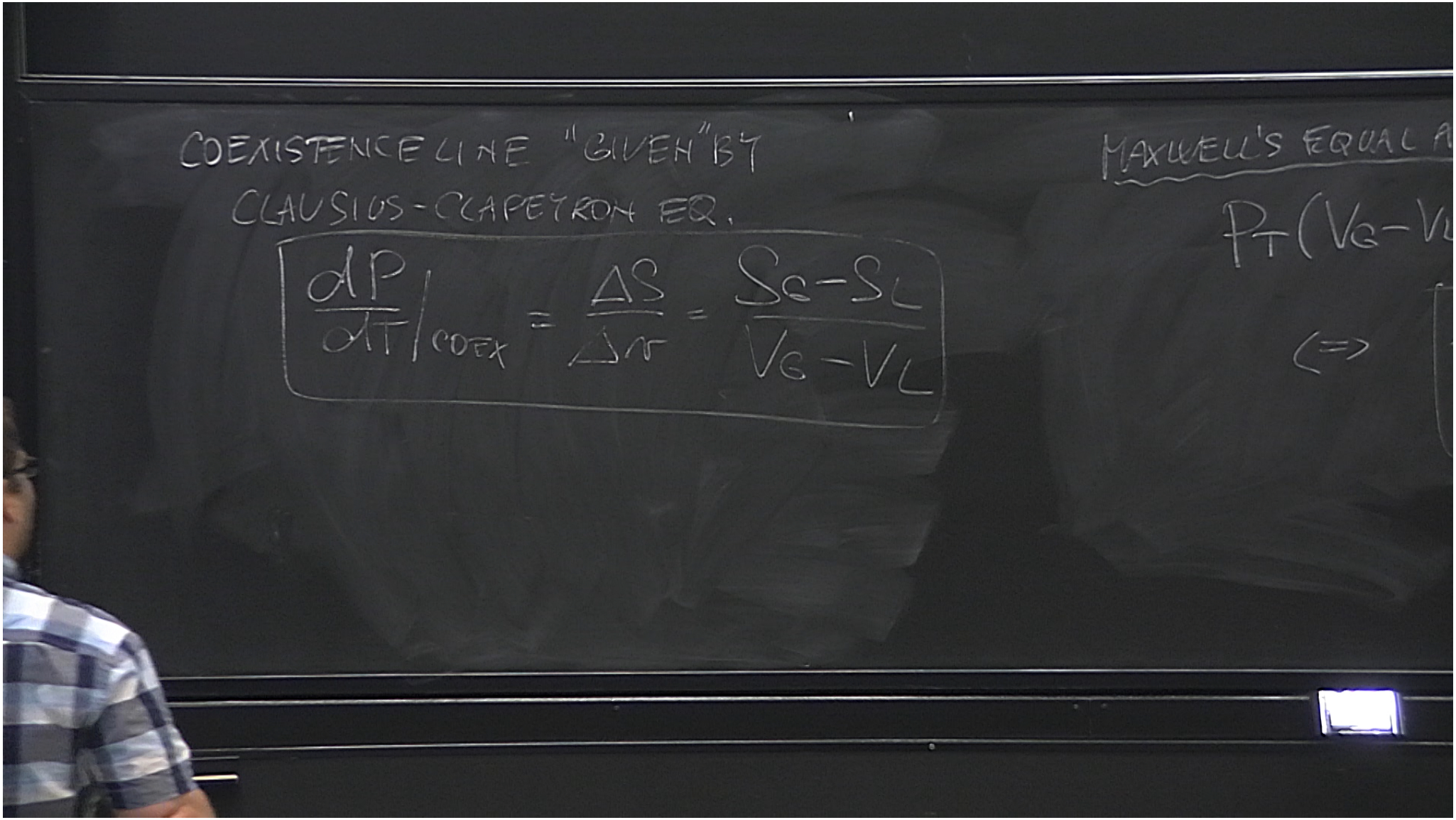

PHASE DIAGRAM
P
T


SECOND (HIGHER)
PHASE
DISCONT.
LIQUID
GAS
P
T


PHASE DIAGRAM
P
T
TPT


SECOND (HIGHER)
G
P
LIQUID
GAS
T
PHASE DIAGRAM
P
COEXISTENCE LINE
LIQUID
GAS
T


SECOND (HIGHER)
G
P
LIQUID
GAS
T
PHASE DIAGRAM
P
CRITICAL POINT
COEXISTENCE LINE
LIQUID
GAS
T


COEXISTENCE LINE "GIVEN" BY
CLAUSIUS-CLAPEYRON EQ.
$\left.\frac{dP}{dT}\right|_{COEX} = \frac{\Delta S}{\Delta V} = \frac{S_G - S_L}{V_G - V_L}$
MAXWELL'S EQUAL A
$P_T(V_G - V_L$
$\Leftrightarrow$

COEXISTENCE LINE "GIVEN" BY

CLAUSIUS-CLAPEYRON EQ.

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

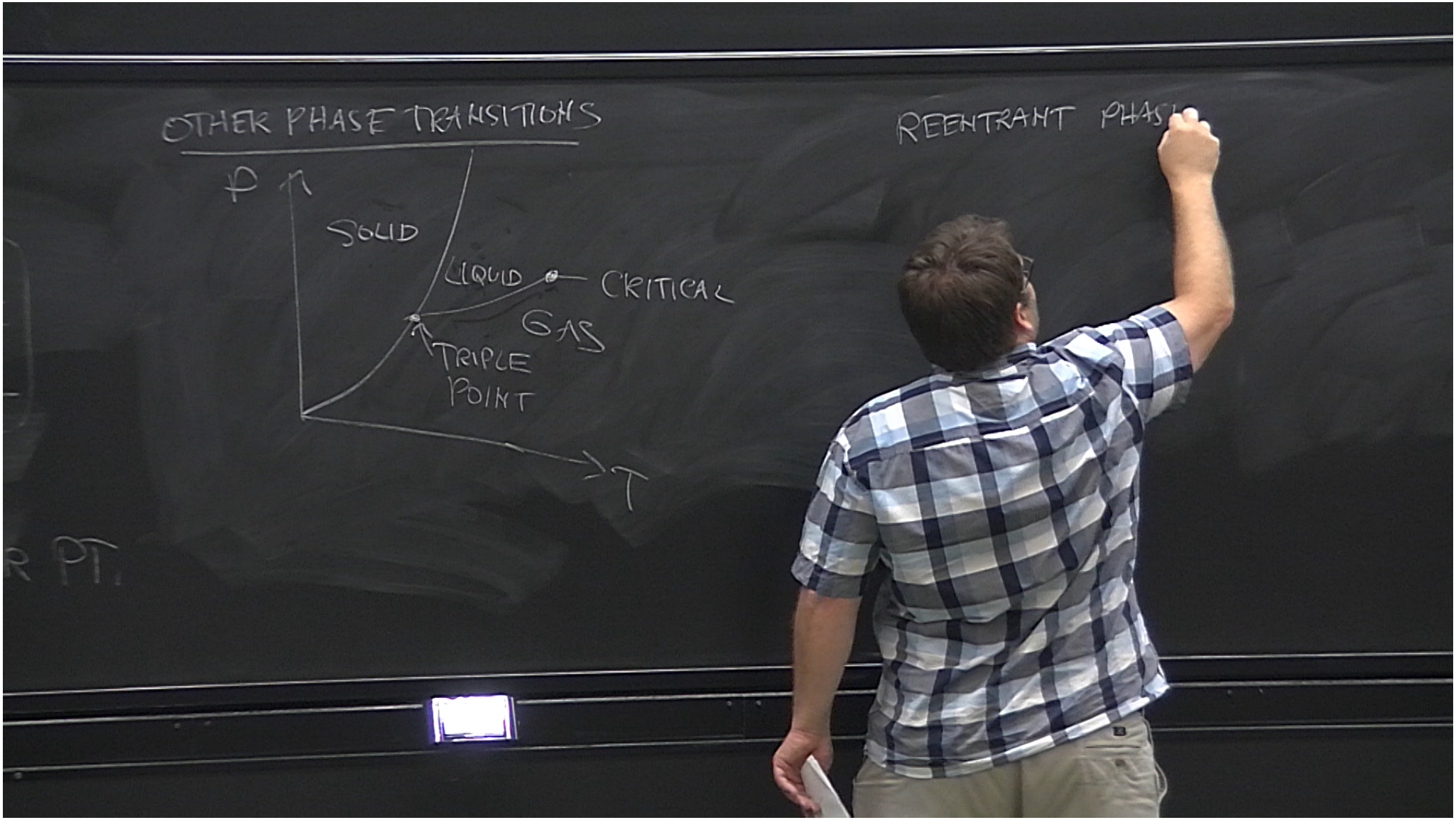
(FIRST-ORDER PTS)

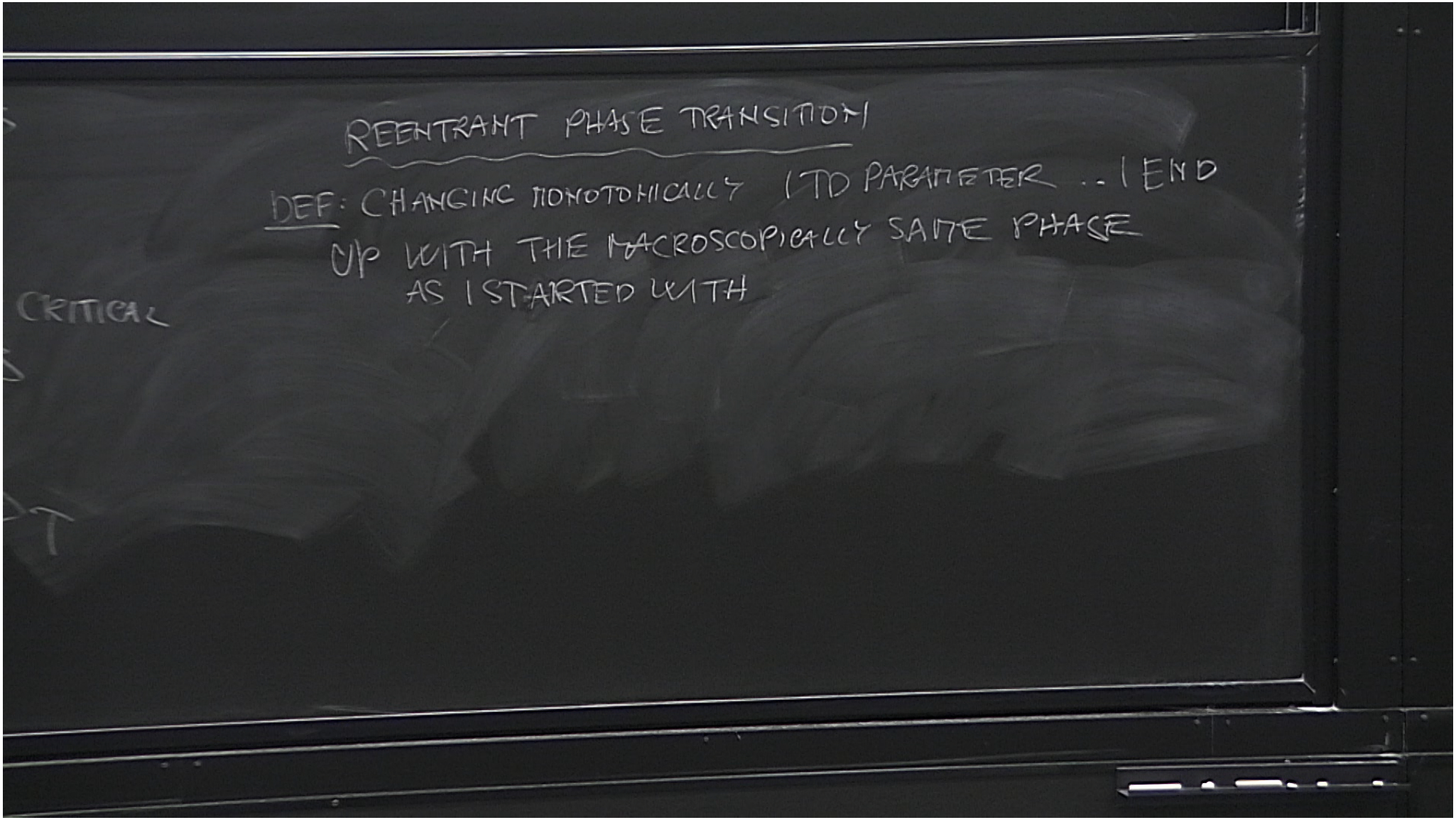
EHRENFEST EQS... 2ND-ORDER PT.

MAXWELL'S EQUAL A

$P_T(V_G - V$

$\Leftrightarrow$

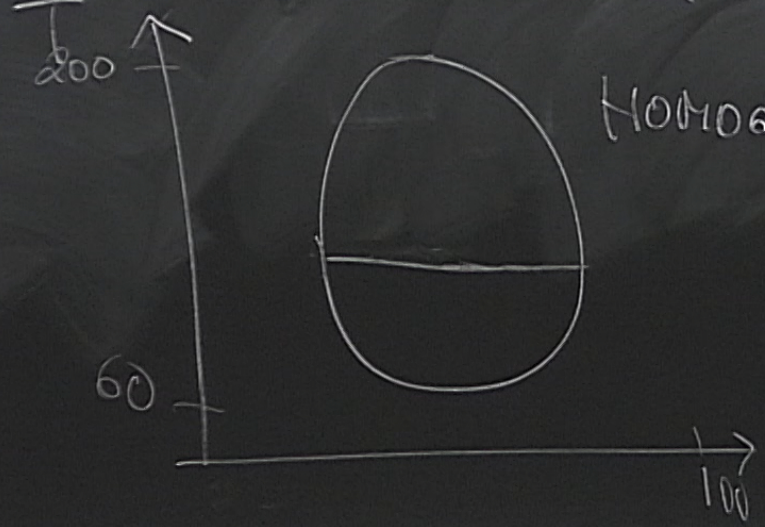

OTHER PHASE TRANSITIONS
P
SOLID
LIQUID
CRITICAL
GAS
TRIPLE
POINT
T
REENTRANT PHAS


REENTRANT PHASE TRANSITION
DEF: CHANGING MONOTONICALLY WITH PARAMETER .. WE END
UP WITH THE MACROSCOPICALLY SAME PHASE
AS WE STARTED WITH
CRITICAL

REENTRANT PHASE TRANSITION

DEF: CHANGING MONOTONICALLY WITH PARAMETER .. WE END UP WITH THE MACROSCOPICALLY SAME PHASE AS WE STARTED WITH (HUDSON - 1904)

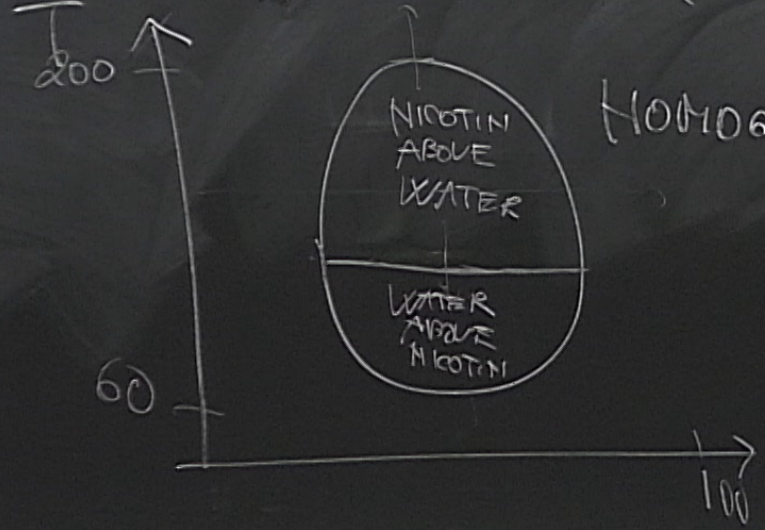
CRITICAL



REENTRANT PHASE TRANSITION

DEF: CHANGING MONOTONICALLY WITH PARAMETER .. WE END UP WITH THE MACROSCOPICALLY SAME PHASE AS WE STARTED WITH (HUDSON - 1904)

CRITICAL



FIRST ORDER

G_{MIN} $\uparrow G_{MIN}$ G_{MIN}

MICROSCOPIC THEORY OF PHASE TRANSITIONS

- MATTER ORGANIZES ITSELF INTO PHASES
  (DIFFERENT MACROSCOPIC PROPERTIES)

EX: • SOLID / LIQUID / GAS — WELL DEFINED INTERFACE

  ↑ RIGIDITY W.R.T. SHEAR

• FERROMAGNET / PARAMAGNET

  $\uparrow \vec{M}$ $\vec{M}=0$

- MACROSCOPIC PROPS (MAGNETIZATION) .. CONSEQUENCE OF ORDERING (EG SPINS)

CANONICAL EXAMPLE : ISING MODEL (LENZ - 1920)

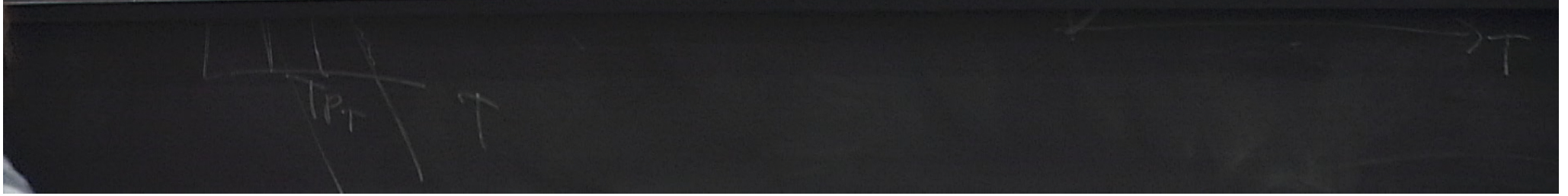
MODEL OF FERROMAGNETISM

1d ... ISING (1925)

2d ... ONSAGER (1944)

3d ... PEOPLE TRYING

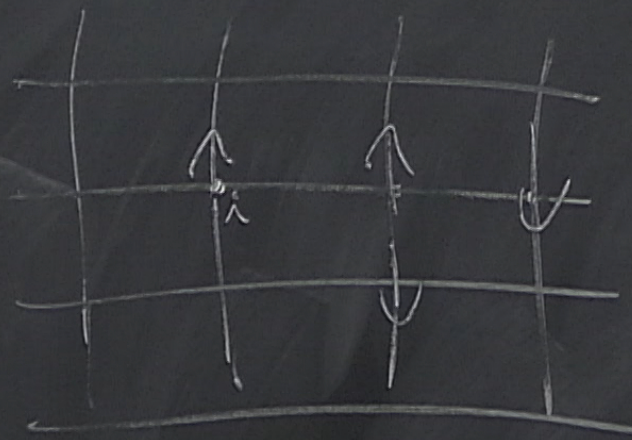
4d & HIGHER IS SIMPLE



CONSEQUENCE

EL (LENZ - 1920)

CUBIC LATTICE



d ... dim OF LATTICE.

SPINS ... UP / DOWN $\quad \sigma_i = \pm 1$

$$H = -\frac{1}{2} \sum_{ij} J_{ij} \sigma_i \sigma_j$$

$J_{ij} > 0$ ... SPINS WANT TO ALIGN.