Title: Statistical Physics Lecture - 112023

Speakers: Emilie Huffman

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Thermodynamic approach to phase transitions

Up till now, we assumed noninteracting particles

- solved models exactly
- Z as products of single-particle expressions

Now when we allow interactions:

- harder to solve
- discontinuities / singularities in thermodynamic functions
- phase transitions!

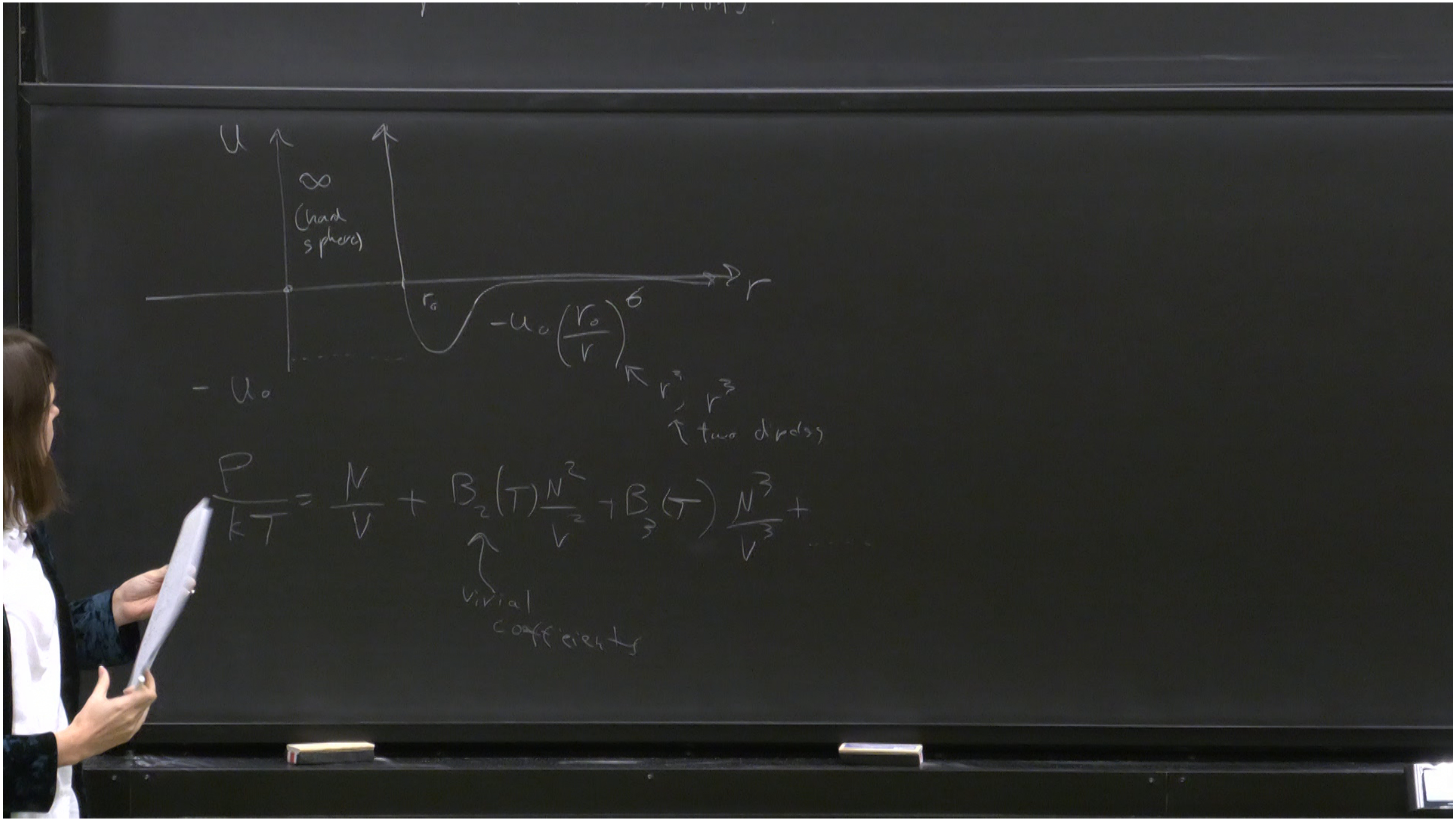
We begin with a thermodynic model, van der Waals gas, defined through:

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

V/N

David Tong's Statistical Physics 2.5

Pathria, 10.1–10.3


U
∞
(hard sphere)
r
r_0
$-u_0\left(\frac{r_0}{r}\right)^6$
$-u_0$
r^3
two dipoles
$\frac{P}{kT} = \frac{N}{V} + B_2(T)\frac{N^2}{V^2} + B_3(T)\frac{N^3}{V^3} + \ldots$
virial coefficients

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

- When $a = 0, b = 0$, $Pv = kT$
- a increases P → interactions between particles increases pressure
- b reduces v → particles now have some volume to them, reduces volume over all

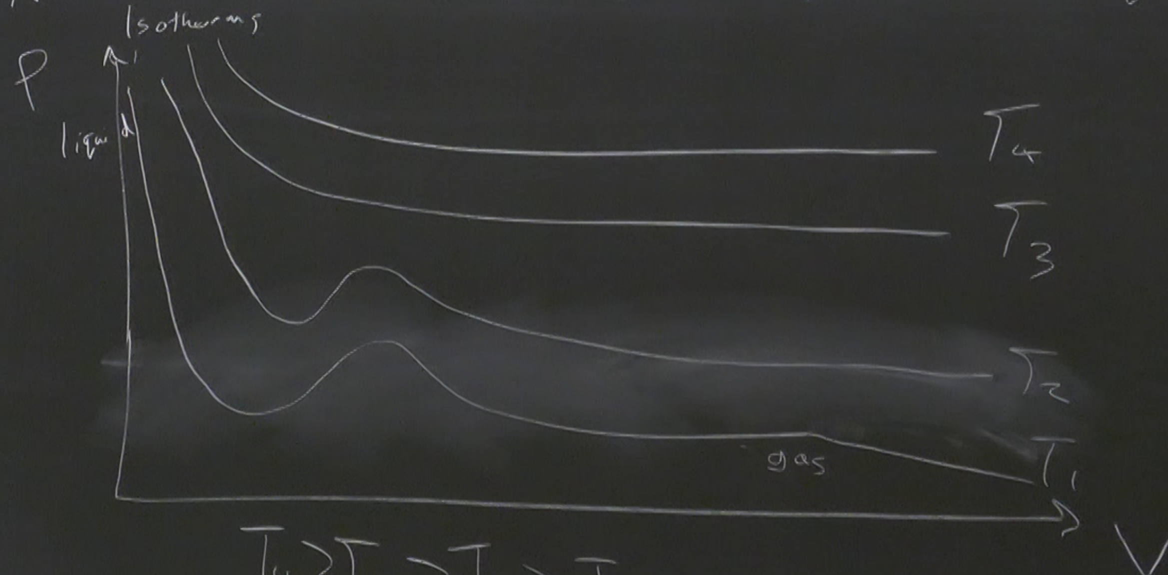
Lennard - Jones potential

$$-u_0\left(\frac{r_0}{r}\right)^6 + u_0\left(\frac{r_0}{r}\right)^{12}$$

les

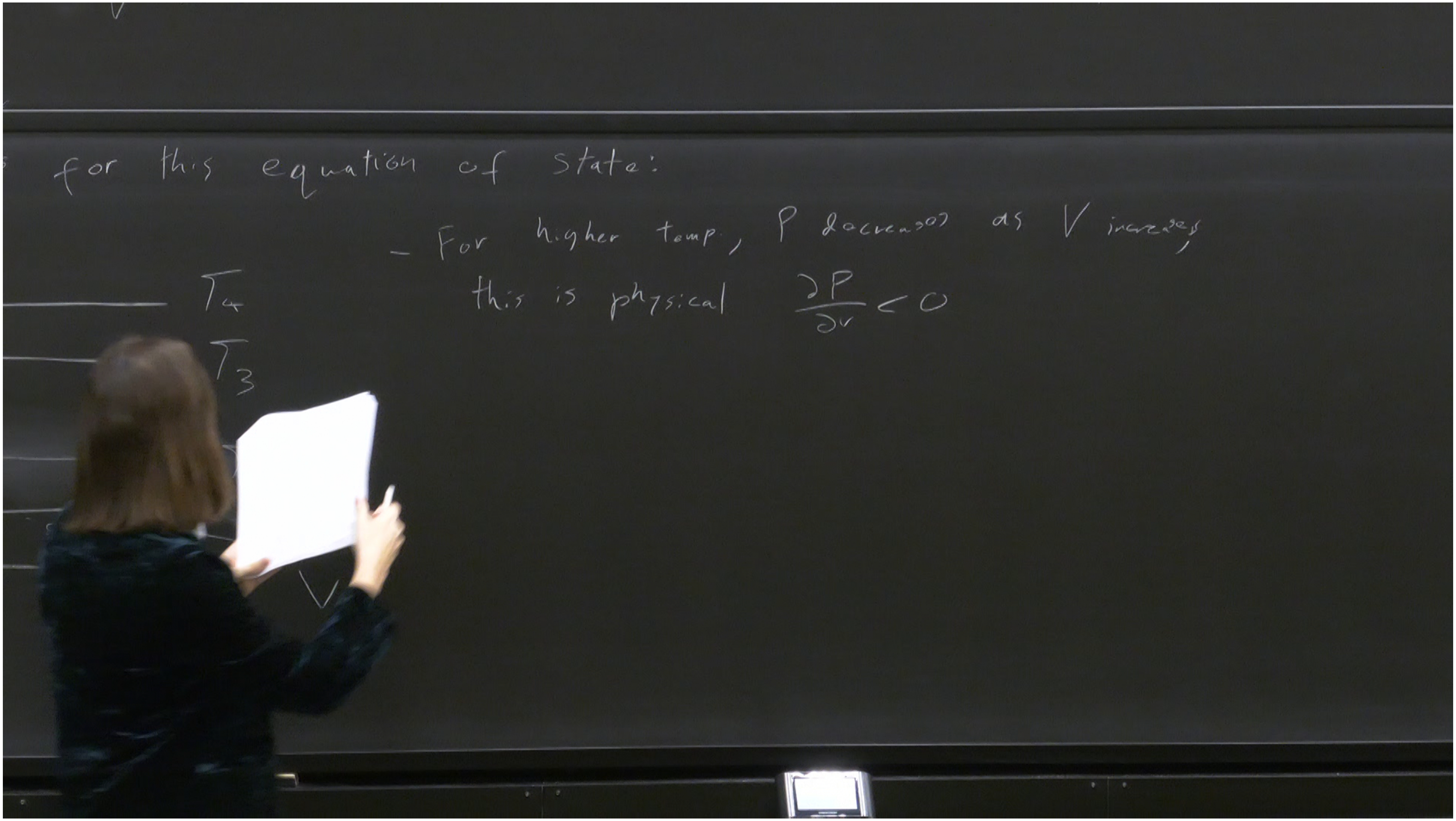
Virial coefficients

- Now let's look at plots for this equation of state:



$T_4 > T_3 > T_2 > T_1$

- For higher temp, P

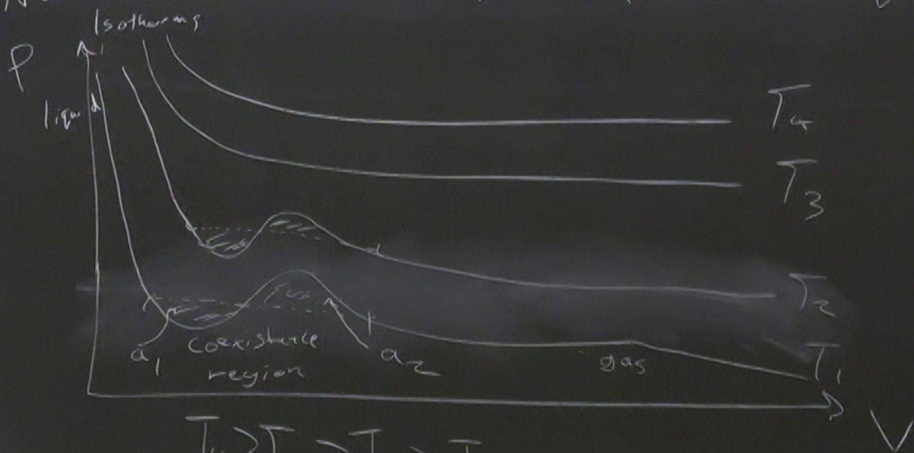

for this equation of state:
- For higher temp., P decreases as V increases,
this is physical $\frac{\partial P}{\partial V} < 0$
T_4
T_3
V

$$\frac{P}{kT} = \frac{N}{V} + B_2(T)\frac{N^2}{V^2} + B_3(T)\frac{N^3}{V^3} + \cdots$$

virial coefficients

volume to them, reduces volume over all

- Now let's look at plots for this equation of state:



$T_4 > T_3 > T_2 > T_1$

$a_1 = a_2$

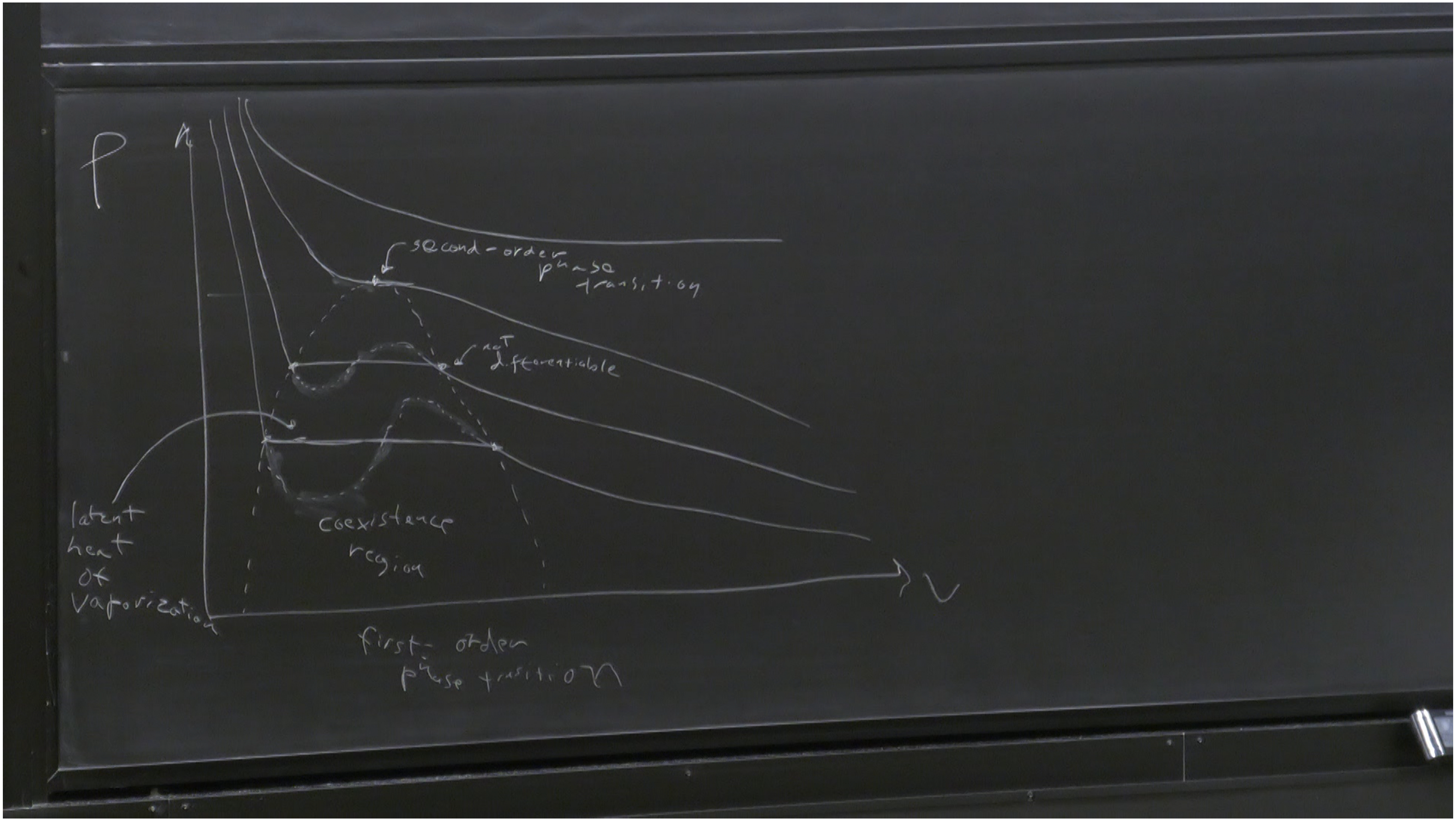
- For higher temp, P decreases as V increases, this is physical $\frac{\partial P}{\partial V} \leq 0$
- For T_2 and T_1, there are uphysical regions

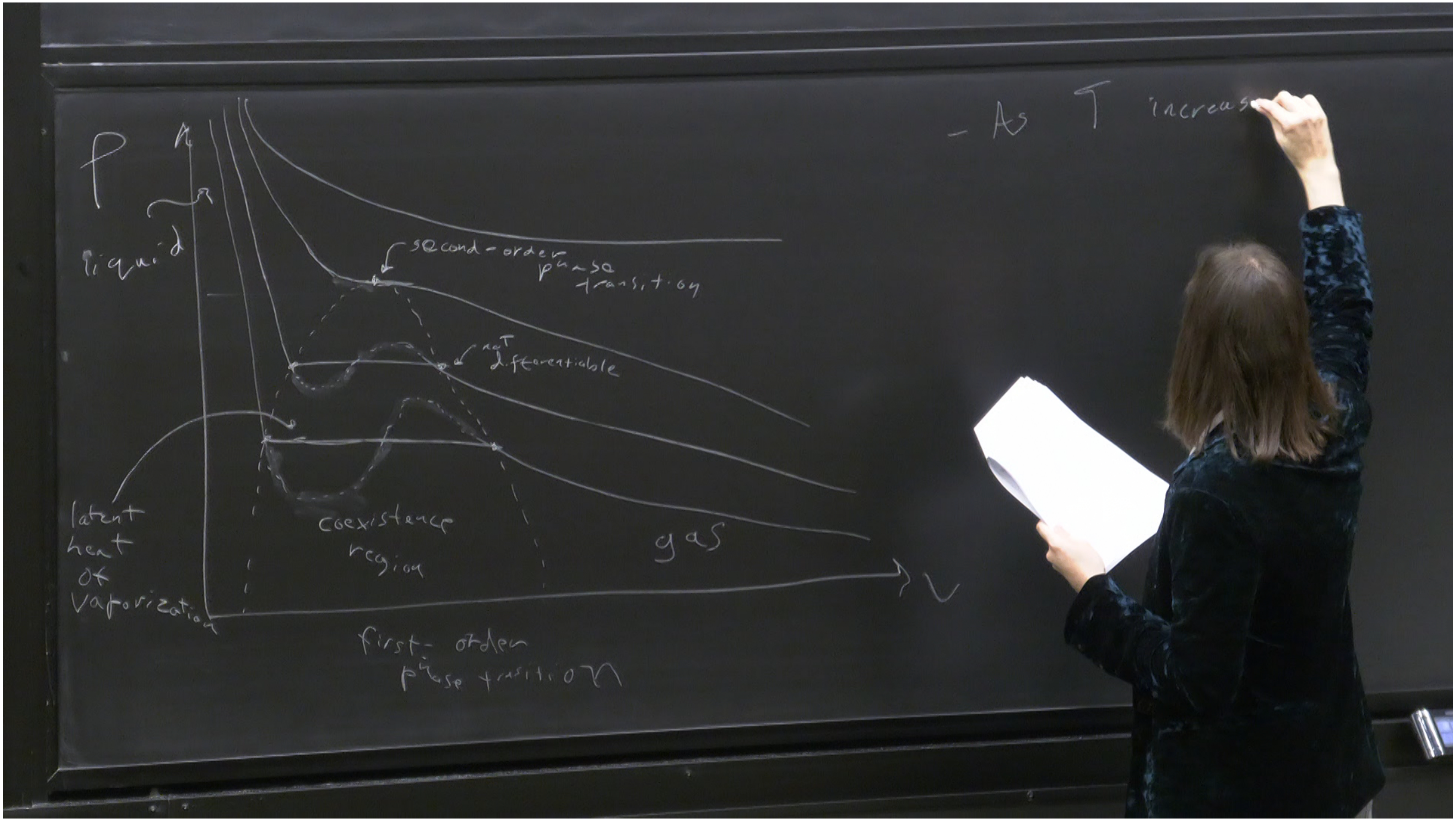
↖ comes from assumption of uniform density

– We can fix these unphysical regions
with the Maxwell construction
of equal areas.

al

iform


P
V
second-order phase transition
not differentiable
latent heat of vaporization
coexistence region
first-order phase transition



- As T increas
P
liquid
second-order
phase
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not
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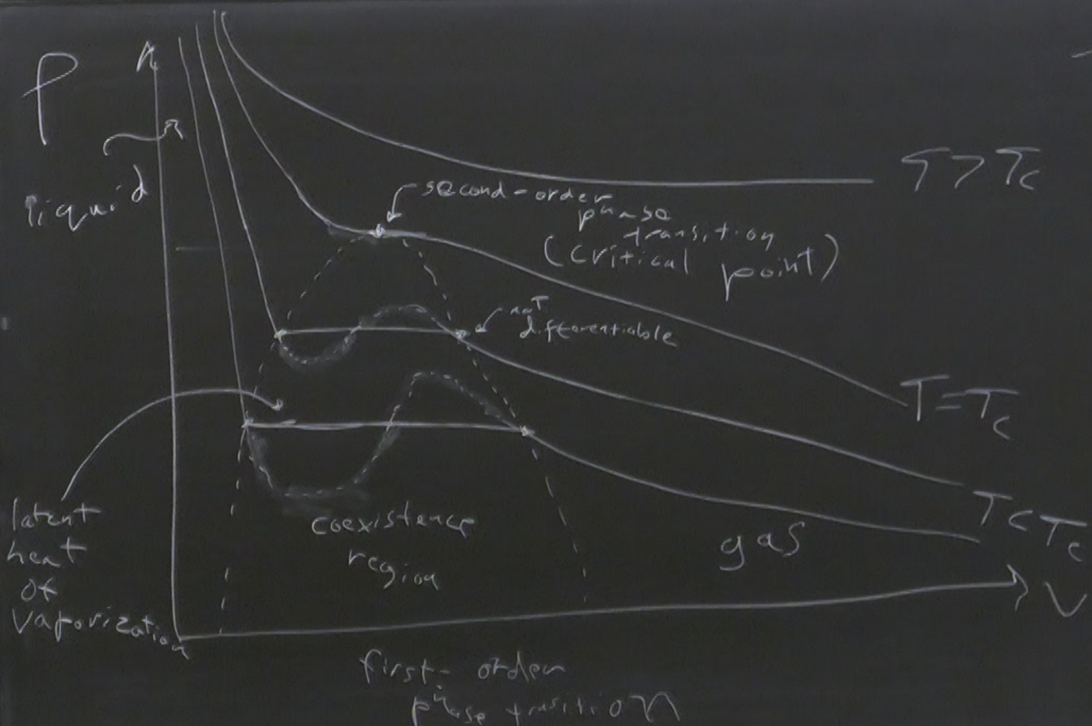


- As T increases, coexistence becomes narrower, collapses to a single point — critical point, with temp. T_c.

- At the critical point,

$$\frac{\partial^2 P}{\partial V^2} = \frac{\partial P}{\partial V} = 0$$

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

$$p = \frac{kT}{v-b} - \frac{a}{v^2}$$

$$\frac{\partial p}{\partial v} =$$

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

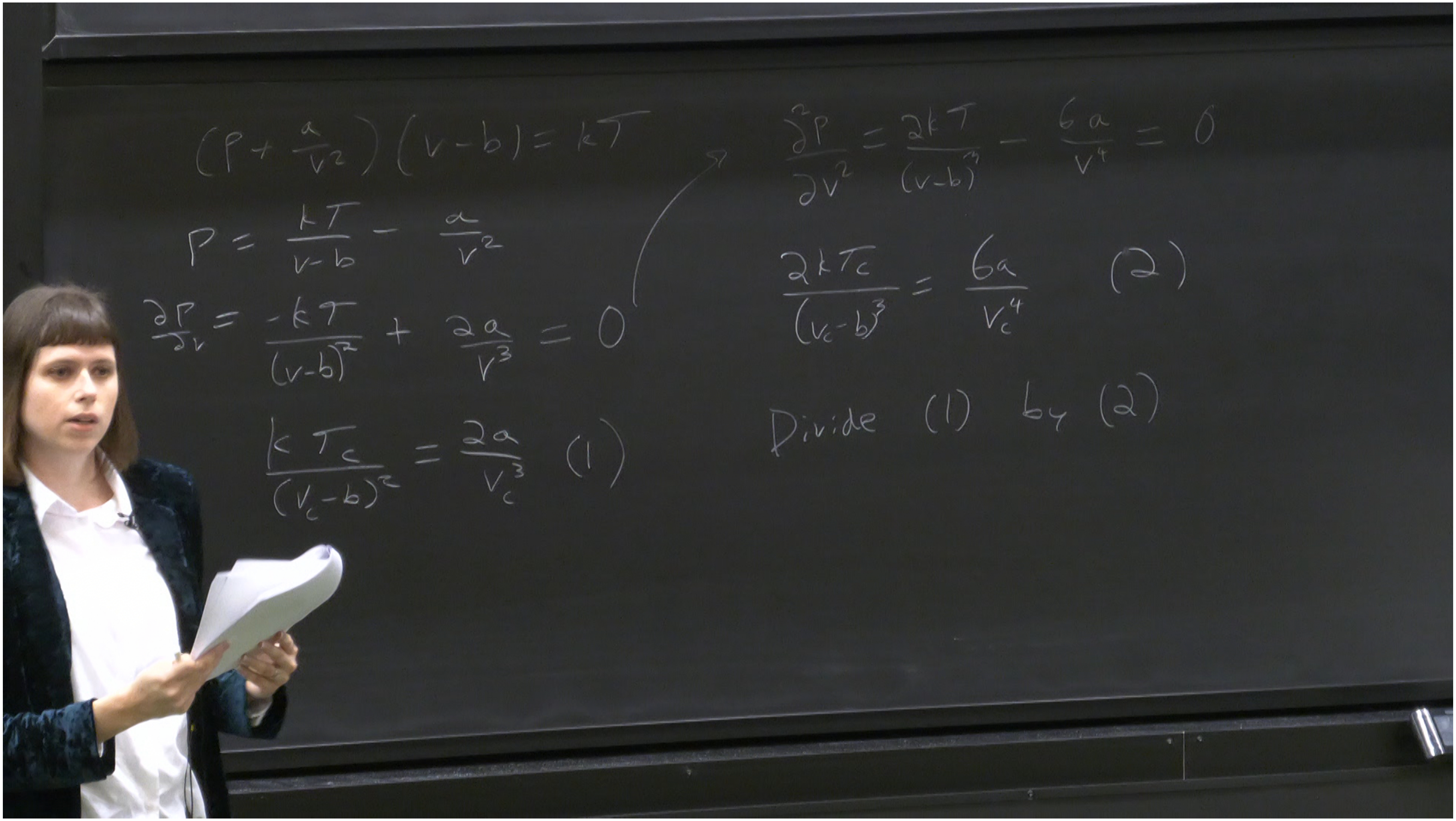
$$P = \frac{kT}{v-b} - \frac{a}{v^2}$$

$$\frac{\partial P}{\partial v} = \frac{-kT}{(v-b)^2} + \frac{2a}{v^3} = 0$$

$$\frac{kT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \quad (1)$$

$$\frac{\partial^2 P}{\partial v^2} = \frac{2kT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

$$\frac{2kT_c}{(v_c - b)^3} = \frac{6a}{v_c^4} \quad (2)$$


$\left(P + \frac{a}{v^2}\right)(v-b) = kT$
$P = \frac{kT}{v-b} - \frac{a}{v^2}$
$\frac{\partial P}{\partial v} = \frac{-kT}{(v-b)^2} + \frac{2a}{v^3} = 0$
$\frac{kT_c}{(V_c-b)^2} = \frac{2a}{V_c^3}$ (1)
$\frac{\partial^2 P}{\partial v^2} = \frac{2kT}{(v-b)^3} - \frac{6a}{v^4} = 0$
$\frac{2kT_c}{(v_c-b)^3} = \frac{6a}{v_c^4}$ (2)
Divide (1) by (2)

phase transition

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

$$P = \frac{kT}{v-b} - \frac{a}{v^2}$$

$$\frac{\partial P}{\partial v} = \frac{-kT}{(v-b)^2} + \frac{2a}{v^3} = 0$$

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$$\frac{\partial^2 P}{\partial v^2} = \frac{2kT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

$$\frac{2kT_c}{(V_c-b)^3} = \frac{6a}{V_c^4} \quad (2)$$

Divide (1) by (2)

$$\frac{V_c-b}{2} = \frac{V_c}{3}$$

$$\frac{V_c}{6} = \frac{b}{2}$$

$$\boxed{V_c = 3b}$$

From (1):

$$\frac{kT_c}{(3b-b)^2} = \frac{2a}{27b^3} \longrightarrow \frac{kT_c}{4b^2} = \frac{2a}{27b^3} \longrightarrow \boxed{T_c = \frac{8a}{27bk}}$$

$$P_c = \frac{kT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{k\,8a/27bk}{2b} - \frac{a}{9b^2} = \frac{2a}{54b^2}$$

$$\boxed{P_c = \frac{a}{27b^2}}$$

region gas density

V

$T_4 > T_3 > T_2 > T_1$

$a_1 = a_2$

What can we learn close to the critical point?

Defining: $P_r = \frac{P}{P_c}$, $v_r = \frac{v}{v_c}$, $T_r = \frac{T}{T_c}$

$$\left(P + \frac{a}{v^2}\right)(v-b) = kT \longrightarrow \left(P_r P_c + \frac{a}{v_r^2 v_c^2}\right)(v_r v_c - b) = k T_r T_c$$

$$\hookrightarrow \left(P_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r$$

we now define

$$\pi,\ \psi,\ t \ll 1$$

so that

$$P_r = 1+\pi,\quad V_r = 1+\psi,\quad T_r = 1+t$$

T_c

$$\left((1+\pi)(1+\psi)^2 + 3\right)\left(3(1+\psi) - 1\right) = 8\underbrace{(1+t)}_{T_r}\underbrace{(1+\psi)^2}_{V_r^2}$$

What can we learn close to the critical point?

Defining: $P_r = \frac{P}{P_c}$, $v_r = \frac{v}{v_c}$, $T_r = \frac{T}{T_c}$

$$\left(P + \frac{a}{v^2}\right)(v-b) = kT \longrightarrow \left(P_r P_c + \frac{a}{v_r^2 v_c^2}\right)(v_r v_c - b) =$$

$$\hookrightarrow \left(P_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r$$

$$(P_r v_r^2 + 3)(3v_r - 1) = 8T_r v_r^2$$

$$(P_r v_r^2 + 3)(3v_r - 1) = 8 T_r v_r^2$$

$$\pi(2 + 7\psi + 8\psi^2 + 3\psi^3) + 3\psi^3 = 8t(1 + 2\psi + \psi^2)$$

– Thinking about pressure close to critical point with $T = T_c$ ($T_r = 1$, $t = 0$), we have

$$\pi = -\frac{3\psi^3}{2 + 7\psi + 8\psi^2 + 3\psi^3}$$

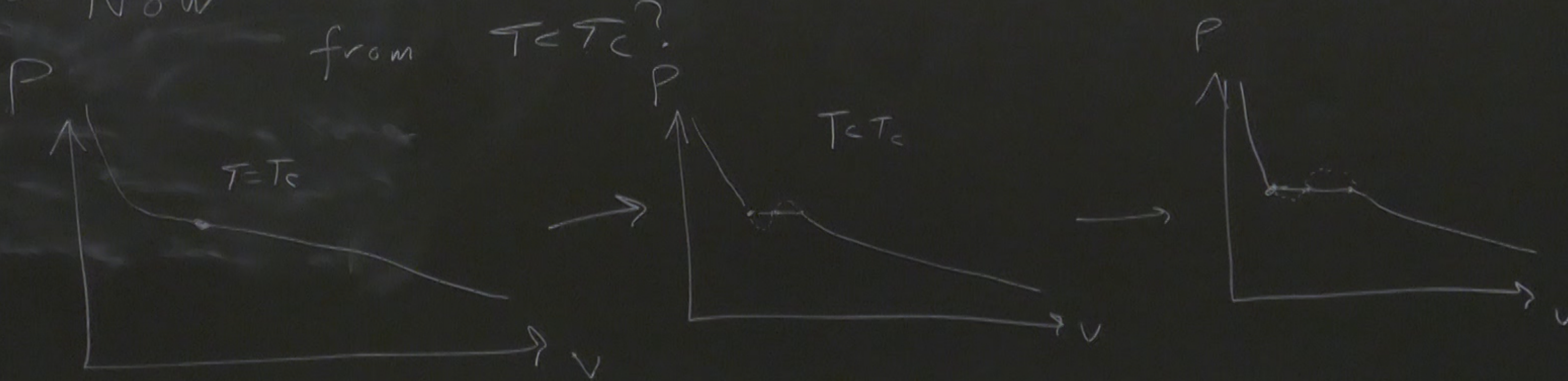
$$(1+x)^{-n} \approx 1 - nx$$

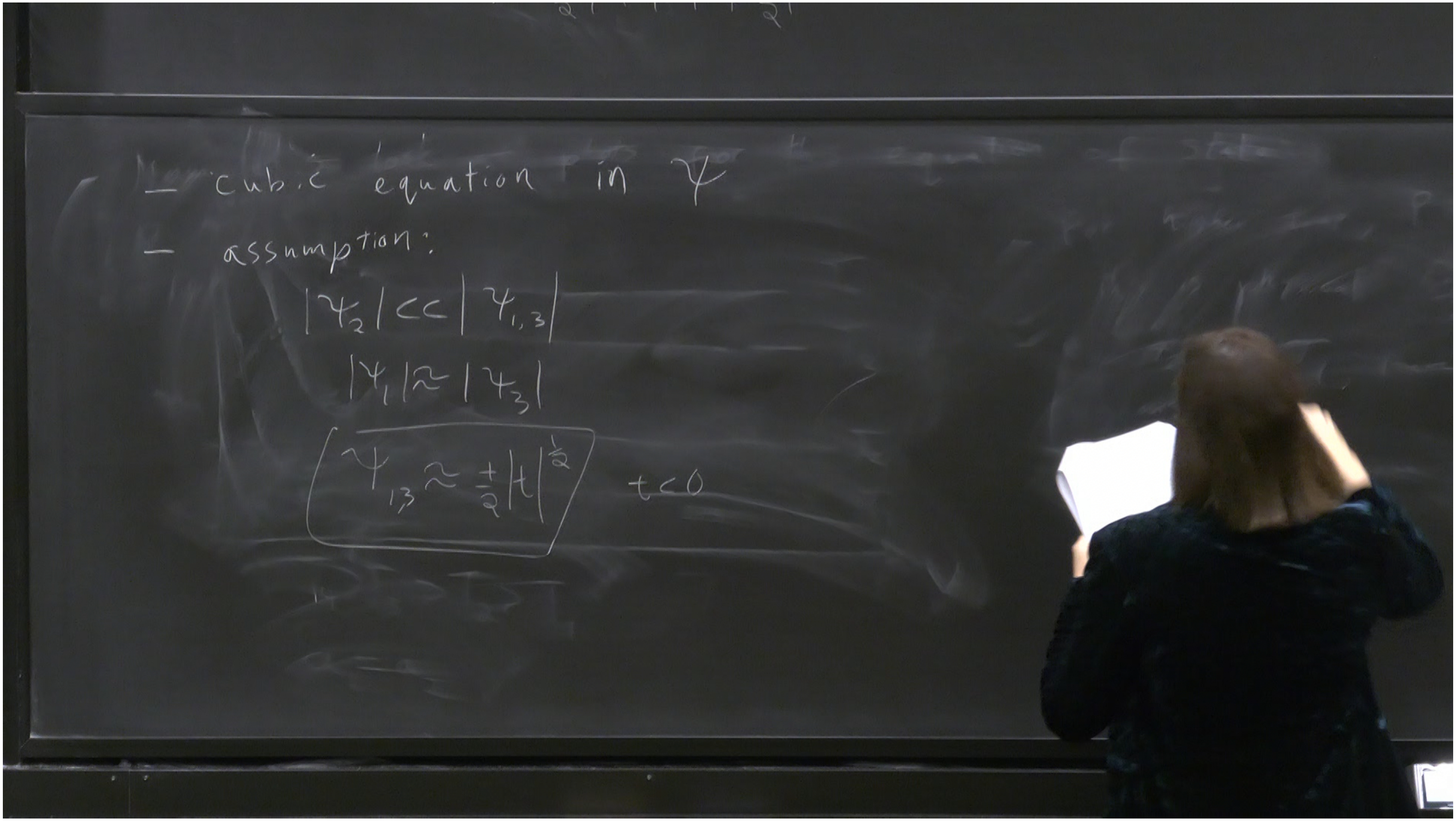
$$= -\frac{\frac{3}{2}\psi^3}{1 + \frac{7}{2}\psi + 4\psi^2 + \frac{3}{2}\psi^3} \approx -\frac{3}{2}\psi^3\left(1 - \frac{7}{2}\psi - 4\psi^2 - \frac{3}{2}\psi^3\right)$$

$$\boxed{\Pi \approx -\frac{3}{2}\psi^3}$$

ΔP ΔV

– Now how does ψ depend on t as we approach from $T<T_c$?




– cubic equation in ψ
– assumption:
$|\psi_2| \ll |\psi_{1,3}|$
$|\psi_1| \approx |\psi_3|$
$\boxed{\psi_{1,3} \approx \pm\frac{1}{2}|t|^{\frac{1}{2}}}$ $t<0$

$\frac{?}{2}y - 4y^2 - \frac{3}{2}y^3 \Big)$

First-order vs. higher order Phase transitions from thermodynamic Perspectives

Ehrenfest: based on Gibbs free energy

$$G = F + PV$$

$$F = U - TS$$

First order: G cont., $\frac{\partial G}{\partial P}$ discont.

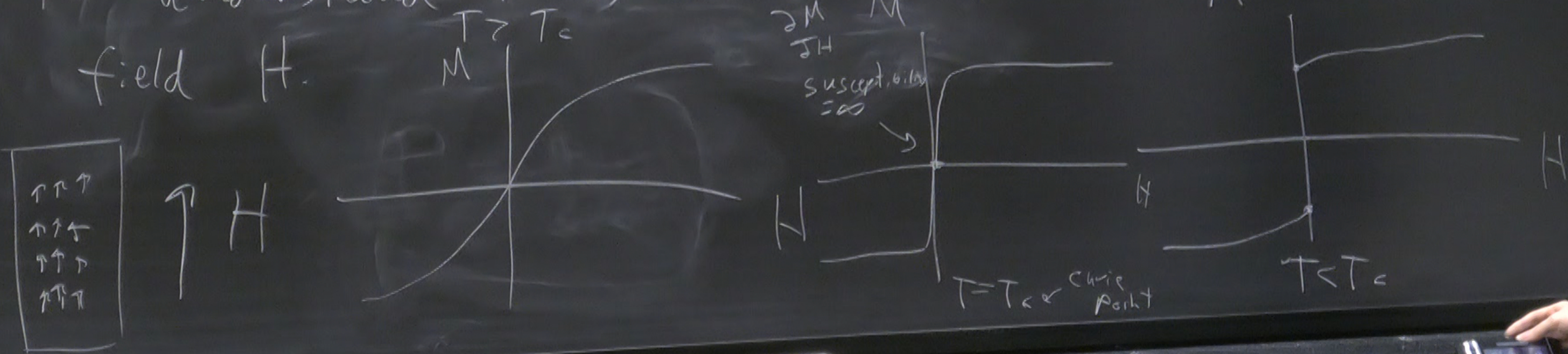
Second order: $G, \frac{\partial G}{\partial P}$ cont, $\frac{\partial^2 G}{\partial P^2}$ discont.

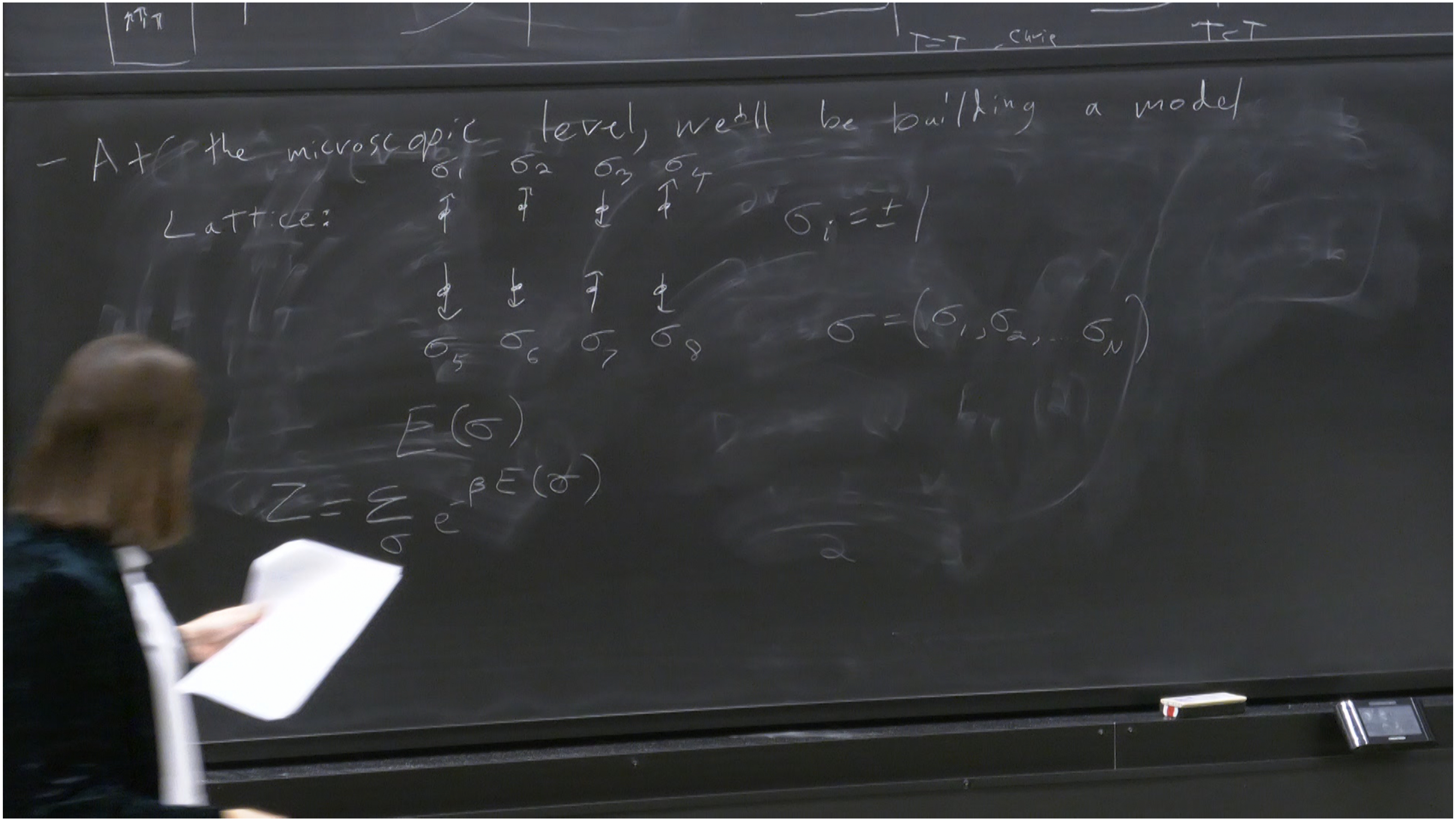
$\vdots$

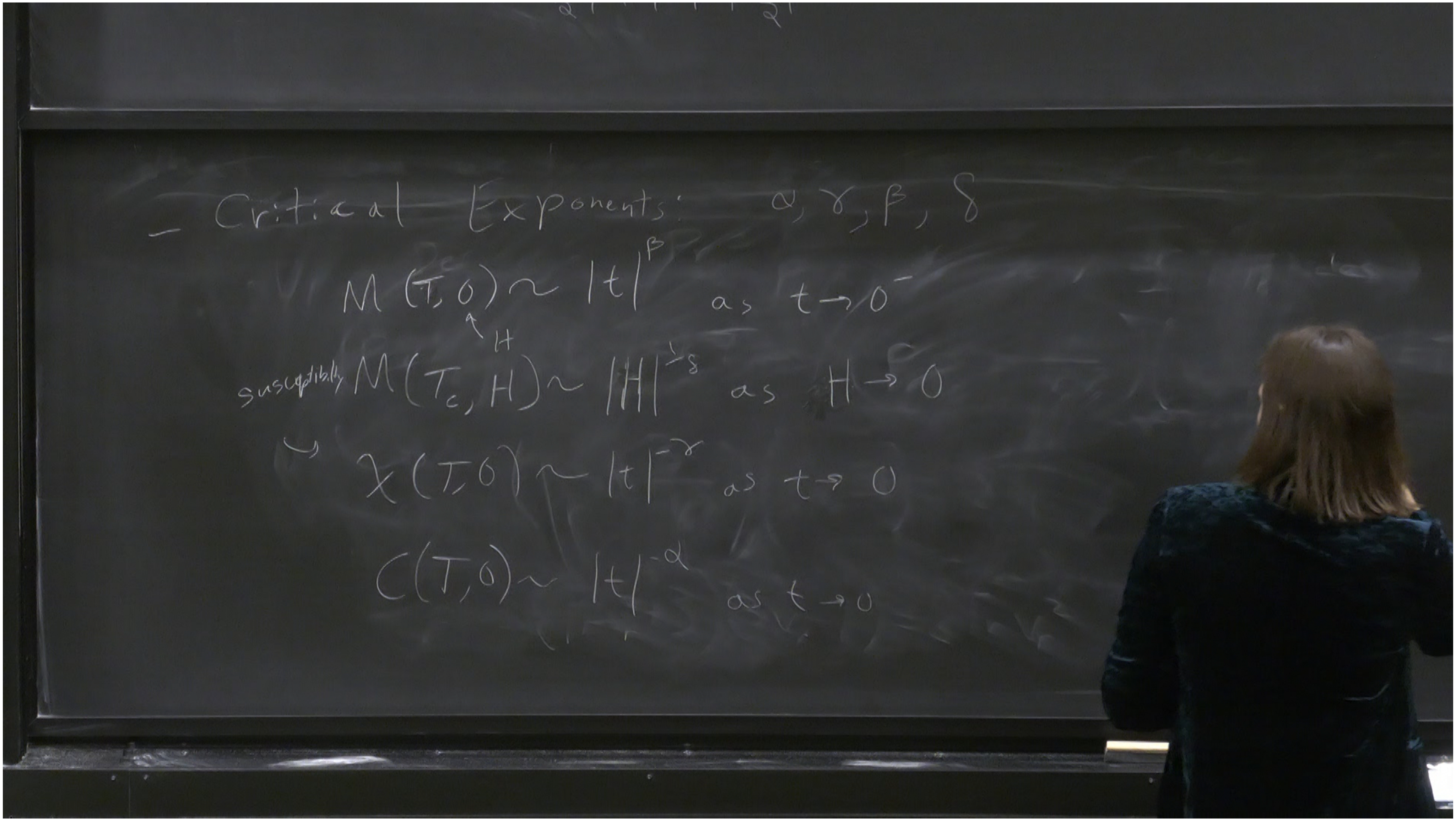
nth order: $G, \frac{\partial G}{\partial P}, \ldots$ cont, $\frac{\partial^n G}{\partial P^n}$ discont.

Microscopic theory of phase transitions

- We have actually just computed two "critical exponents" for the second-order phase transition.
- To understand these, consider a ferromagnet in magnetic field H.




- At the microscopic level, we'll be building a model
Lattice:
σ1 σ2 σ3 σ4
σ5 σ6 σ7 σ8
σi = ±1
σ = (σ1, σ2, ... σN)
E(σ)
Z = Σσ e^(-βE(σ))


- Critical Exponents: $\alpha, \gamma, \beta, \delta$
$M(T,0) \sim |t|^{\beta}$ as $t \to 0^-$
H
susceptibility $M(T_c, H) \sim |H|^{1/\delta}$ as $H \to 0$
$\chi(T,0) \sim |t|^{-\gamma}$ as $t \to 0$
$C(T,0) \sim |t|^{-\alpha}$ as $t \to 0$

$\gamma, \gamma', \alpha, \alpha'$

can be different on both sides of a transition

Léonard, Delamotte PRL 115, 200601 (2015)

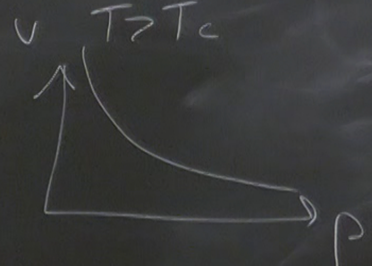
$\gamma, \gamma', \alpha, \alpha'$

can be different on both sides of a transition

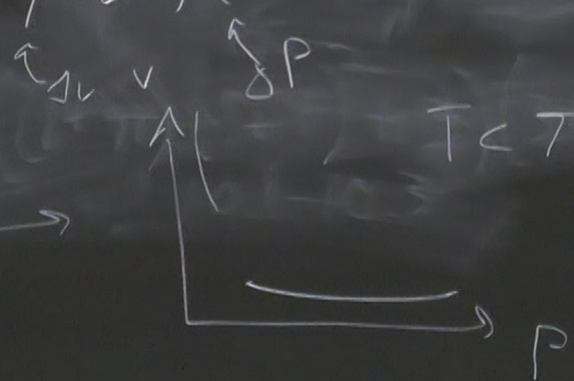
Léonard, Delamotte PRL 115, 200601 (2015)

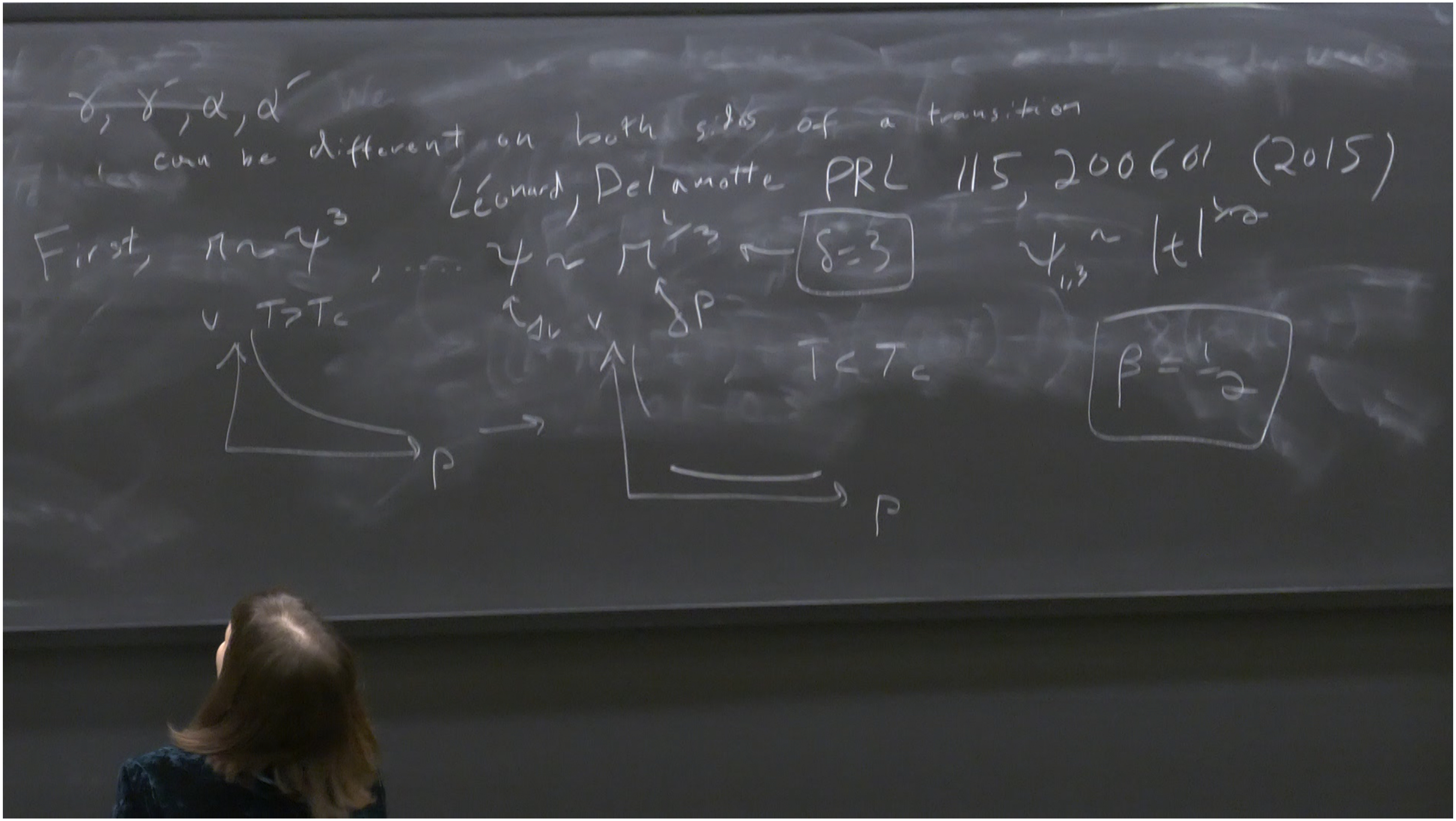
First, $\Pi \sim \psi^3$, ... $\psi \sim \Pi^{1/3}$

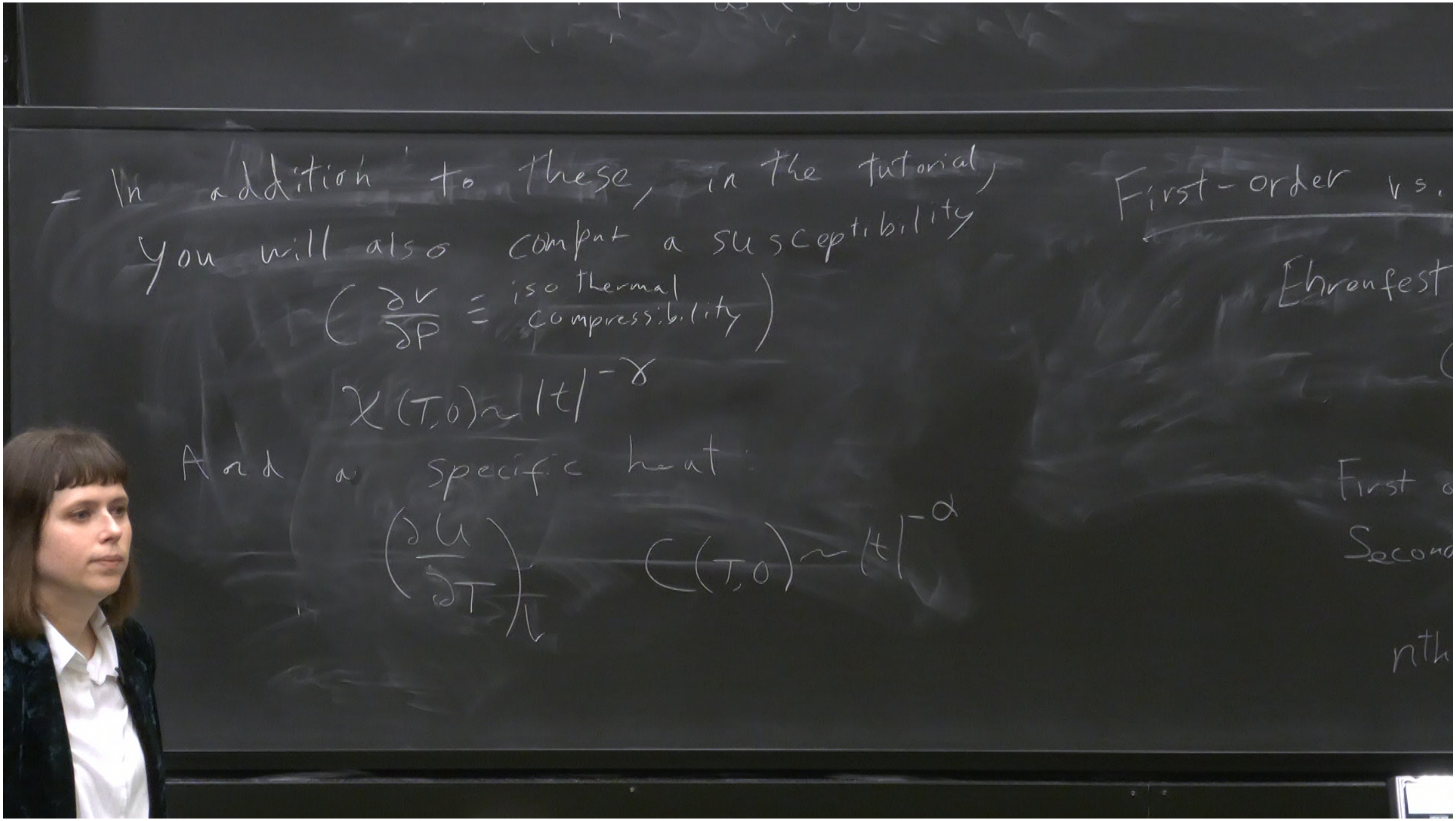
$T > T_c$



$T < T_c$




γ, γ′, α, α′
can be different on both sides of a transition
Léonard, Delamotte PRL 115, 200601 (2015)
First, μ ~ ψ³
ψ ~ μ^{1/3}
δ=3
ψ_{1,3} ~ |t|^{1/2}
v T>Tc
p
δp
T<Tc
β=1/2
p


- In addition to these, in the tutorial,
you will also compute a susceptibility
$\left(\frac{\partial V}{\partial P} \equiv \text{isothermal compressibility} \right)$
$\chi(T,0) \sim |t|^{-\gamma}$
And a specific heat:
$\left(\frac{\partial U}{\partial T} \right)_V$
$C(T,0) \sim |t|^{-\alpha}$
First-order vs.
Ehrenfest
First
Second
nth