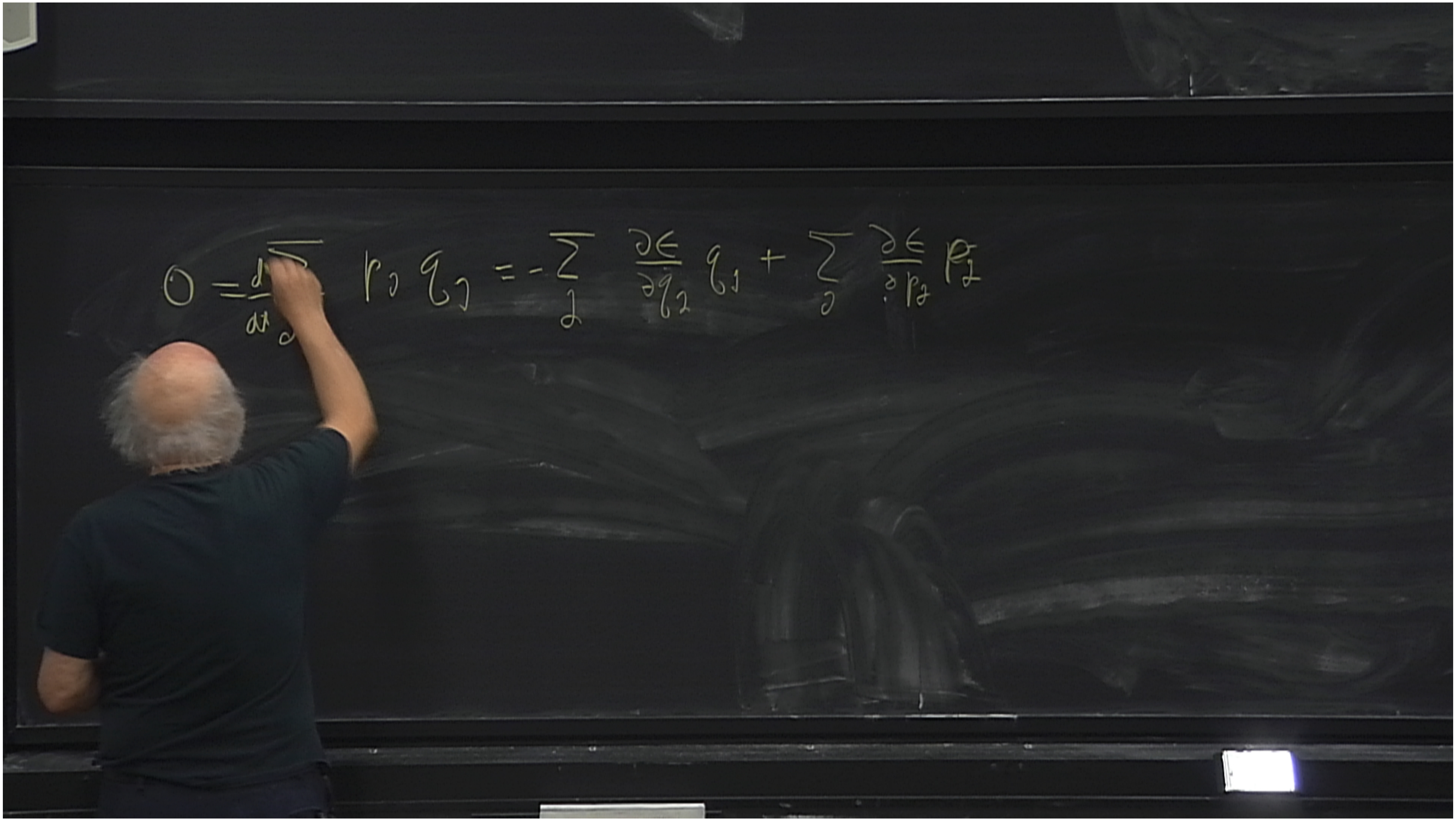
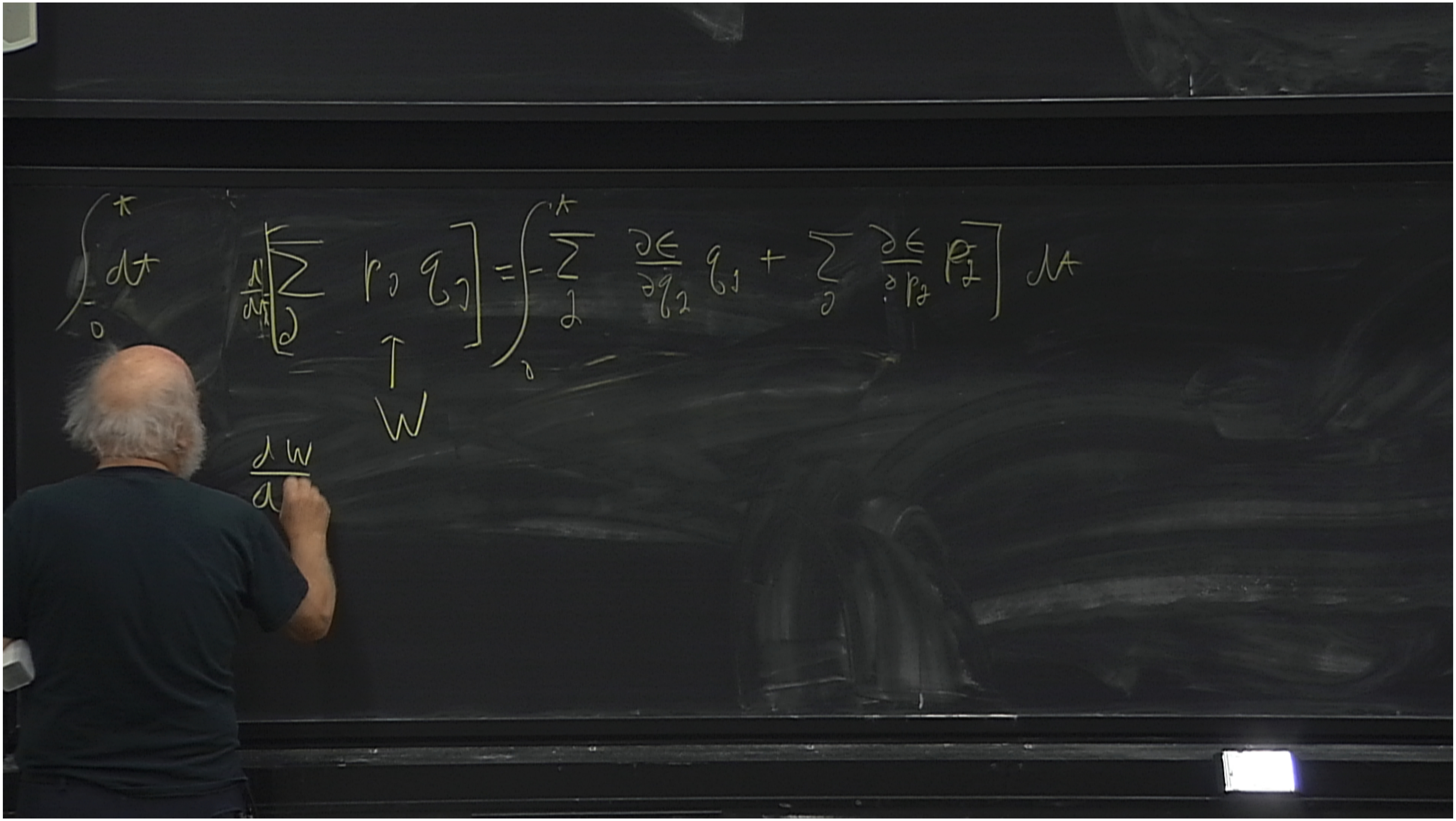
Title: Statistical Mechanics - Lecture 11

Date: Oct 18, 2011 10:30 AM

URL: http://pirsa.org/11100040

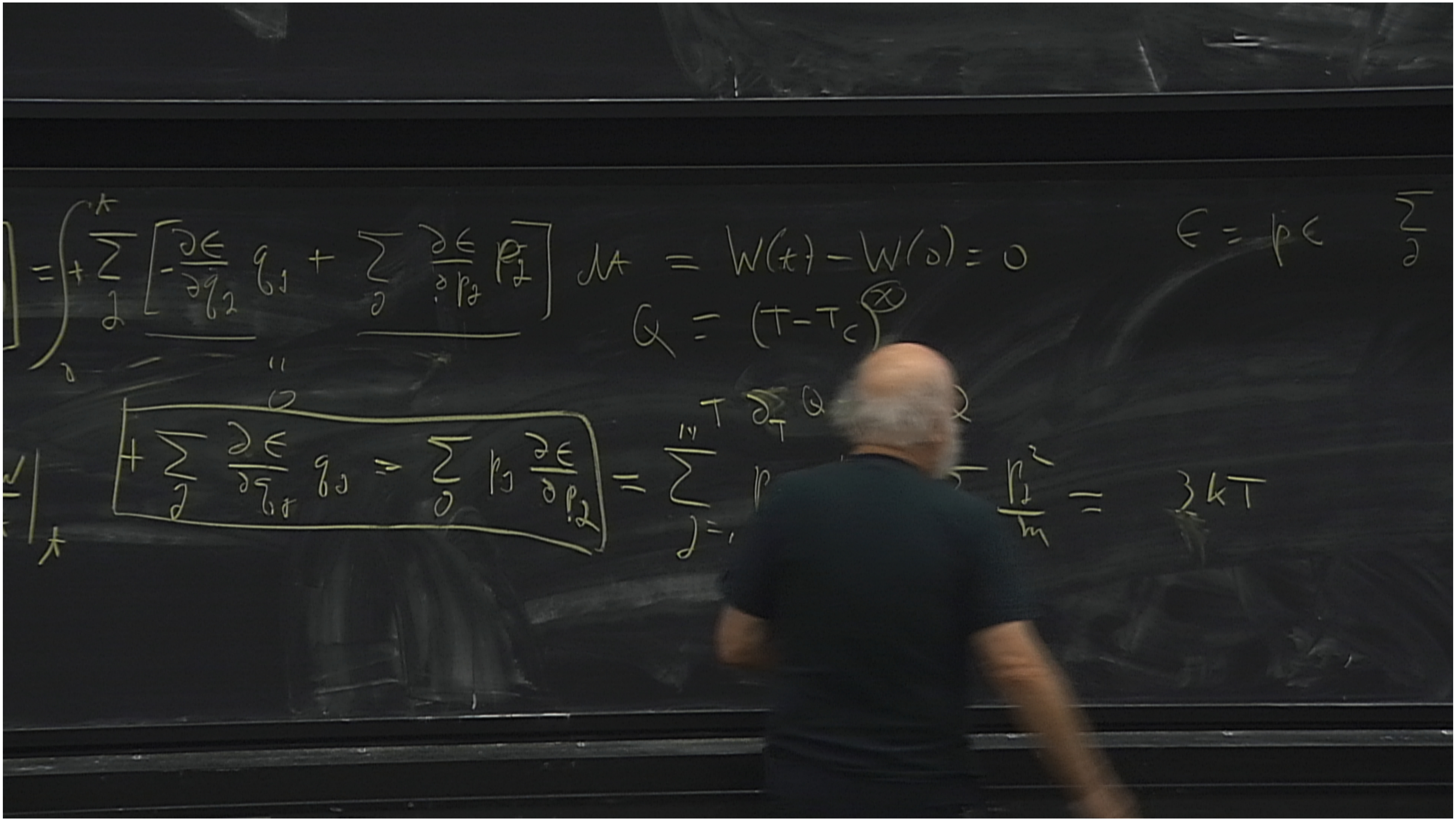
Abstract:

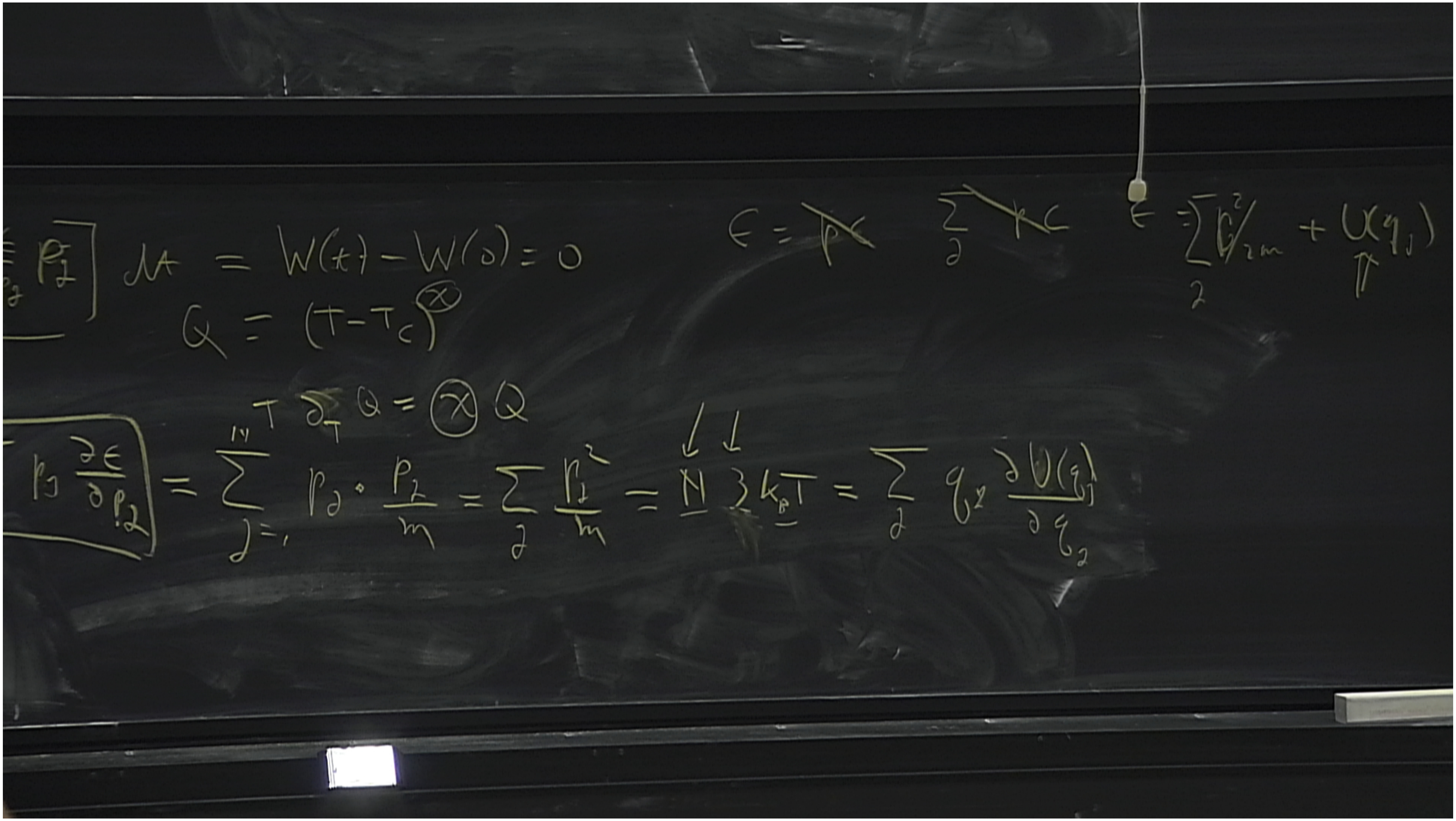

$0 = \frac{d}{dt} \sum_j p_j q_j = -\sum_j \frac{\partial E}{\partial q_j} q_j + \sum_j \frac{\partial E}{\partial p_j} p_j$

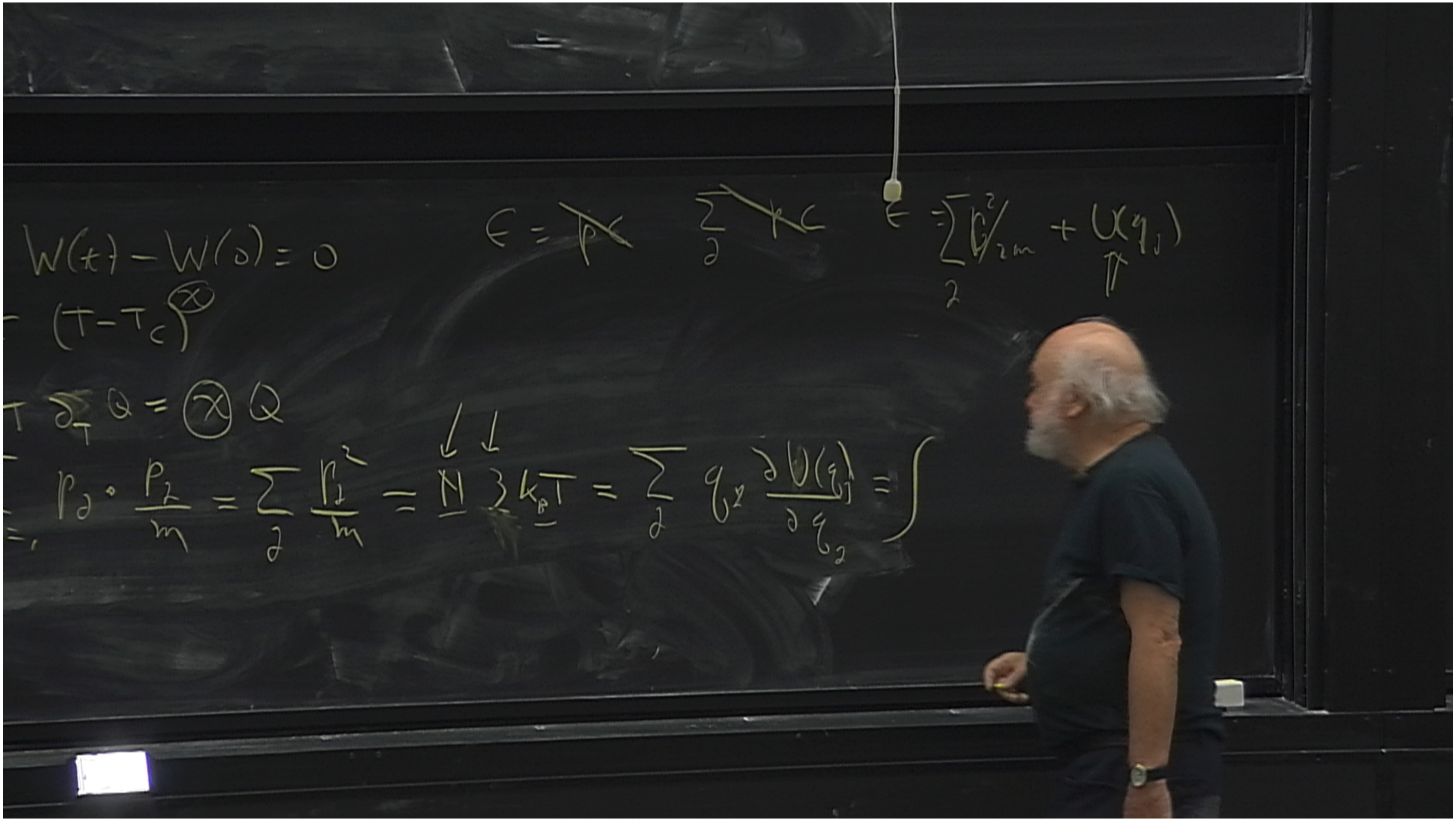

$\int_0^\tau dt \; \frac{d}{dt}\left[\sum_j p_j q_j\right] = \int_0^\tau \left[-\sum_j \frac{\partial E}{\partial q_j} q_j + \sum_j \frac{\partial E}{\partial p_j} p_j\right] dt$
W
$\frac{dW}{d}$

$$\int_0^t dt \, \frac{d}{dt}\Big[\underbrace{\sum_j p_j q_j}_{W}\Big] = \int_0^t + \sum_j \Big[-\frac{\partial \epsilon}{\partial q_j} q_j + \sum_j \frac{\partial \epsilon}{\partial p_j} p_j \Big] dt = W(t) - W(0) =$$

$$\left.\frac{dW}{dt}\right|_0 = \left.\frac{dW}{dt}\right|_t \qquad \boxed{+\sum_j \frac{\partial \epsilon}{\partial q_j} q_j - \sum_j p_j \frac{\partial \epsilon}{\partial p_j}} = 0$$


= W(t) - W(0) = 0
Q = (T - T_c)
3kT

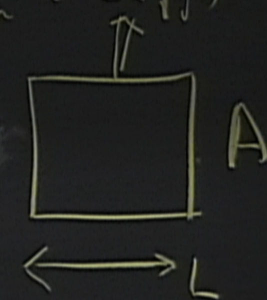

$\mathcal{A} = W(t) - W(0) = 0$
$Q = (T - T_c)^{x}$
$T \partial_T Q = x Q$
$E = \sum_j \left[p_j^2/2m + U(q_j) \right]$
$p_j \frac{\partial E}{\partial p_j} = \sum_{j=1}^{N} p_j \cdot \frac{p_j}{m} = \sum_j \frac{p_j^2}{m} = N\, 3 k_B T = \sum_j q_j \frac{\partial U(q_j)}{\partial q_j}$


W(t) − W(0) = 0

$$W(t) - W(0) = 0 \qquad E = \cancel{pc} \qquad \sum_i \cancel{pc} \qquad E = \sum_i p_i^2/2m + U(q_i)$$

$$(T - T_c)^{x}$$

$$T\,\partial_T Q = x\,Q$$



$$p_i \cdot \frac{p_i}{m} = \sum_i \frac{p_i^2}{m} = N\,3k_BT = \sum_i q_i \cdot \frac{\partial U(q)}{\partial q_i} =$$

$E = \cancel{pc} \quad \sum_j \cancel{pc} \quad E = \sum_j p_j^2/2m + U(q_j)$

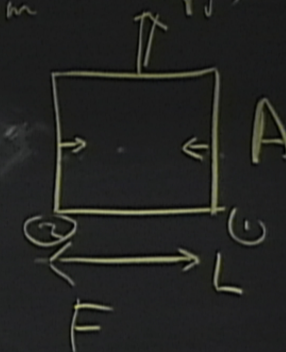
$W(t) - W(0) = 0$

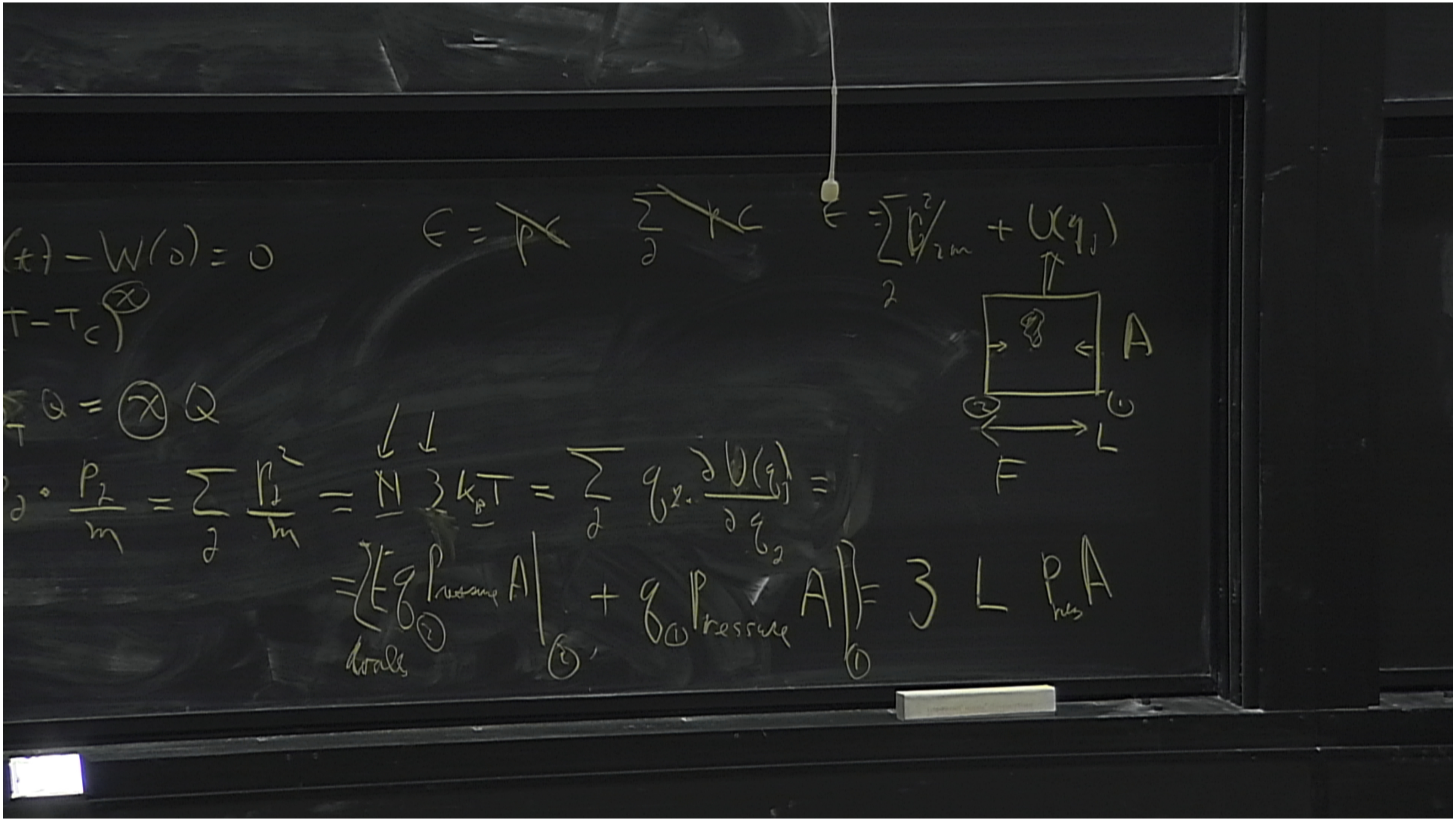
$\sim (T - T_c)^{x}$

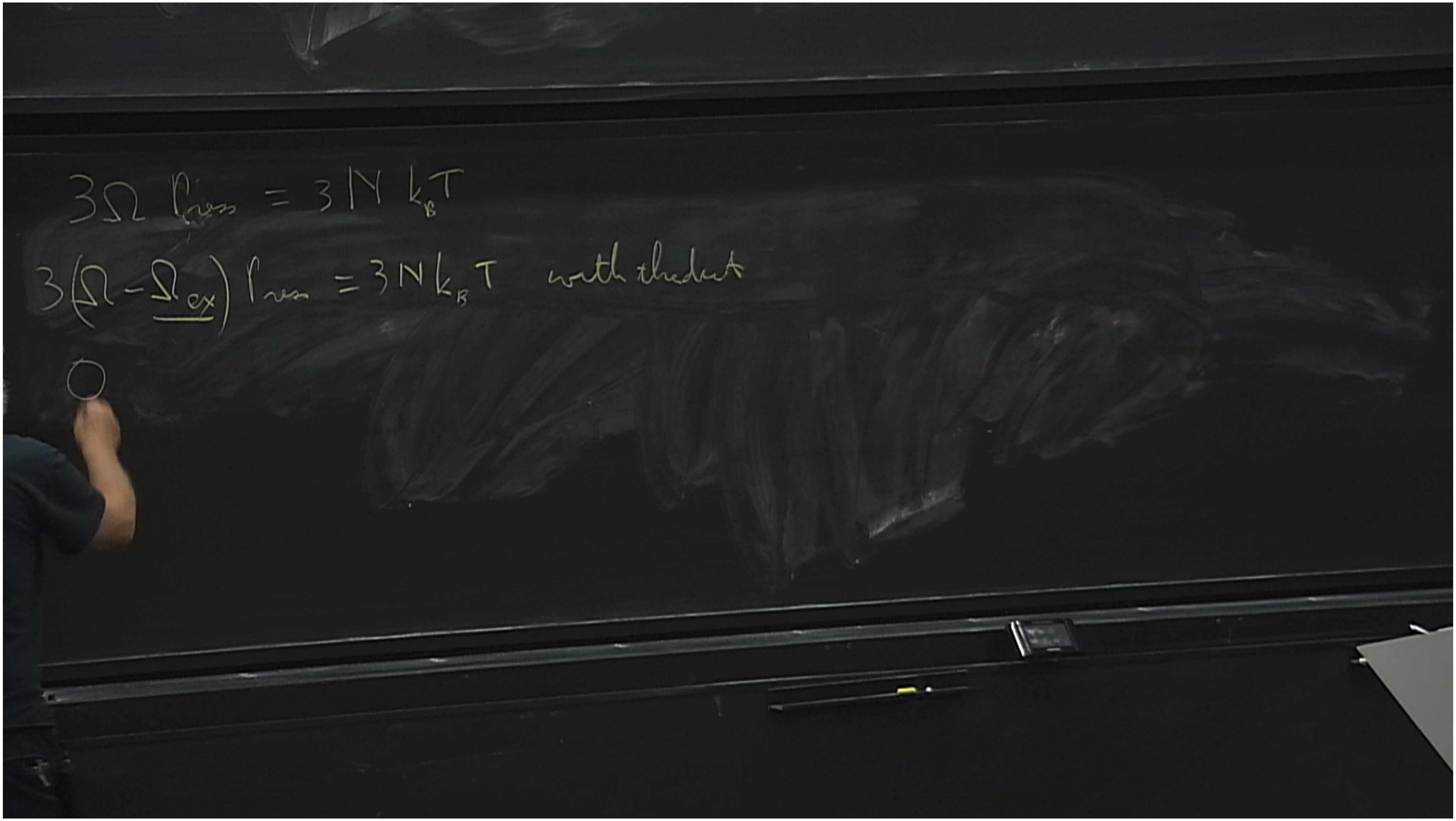
$T\,\partial_T Q = x\, Q$

$p_j \cdot \frac{p_j}{m} = \sum_j \frac{p_j^2}{m} = N\, 3 k_B T = \sum_j q_j \frac{\partial U(q)}{\partial q_j} =$

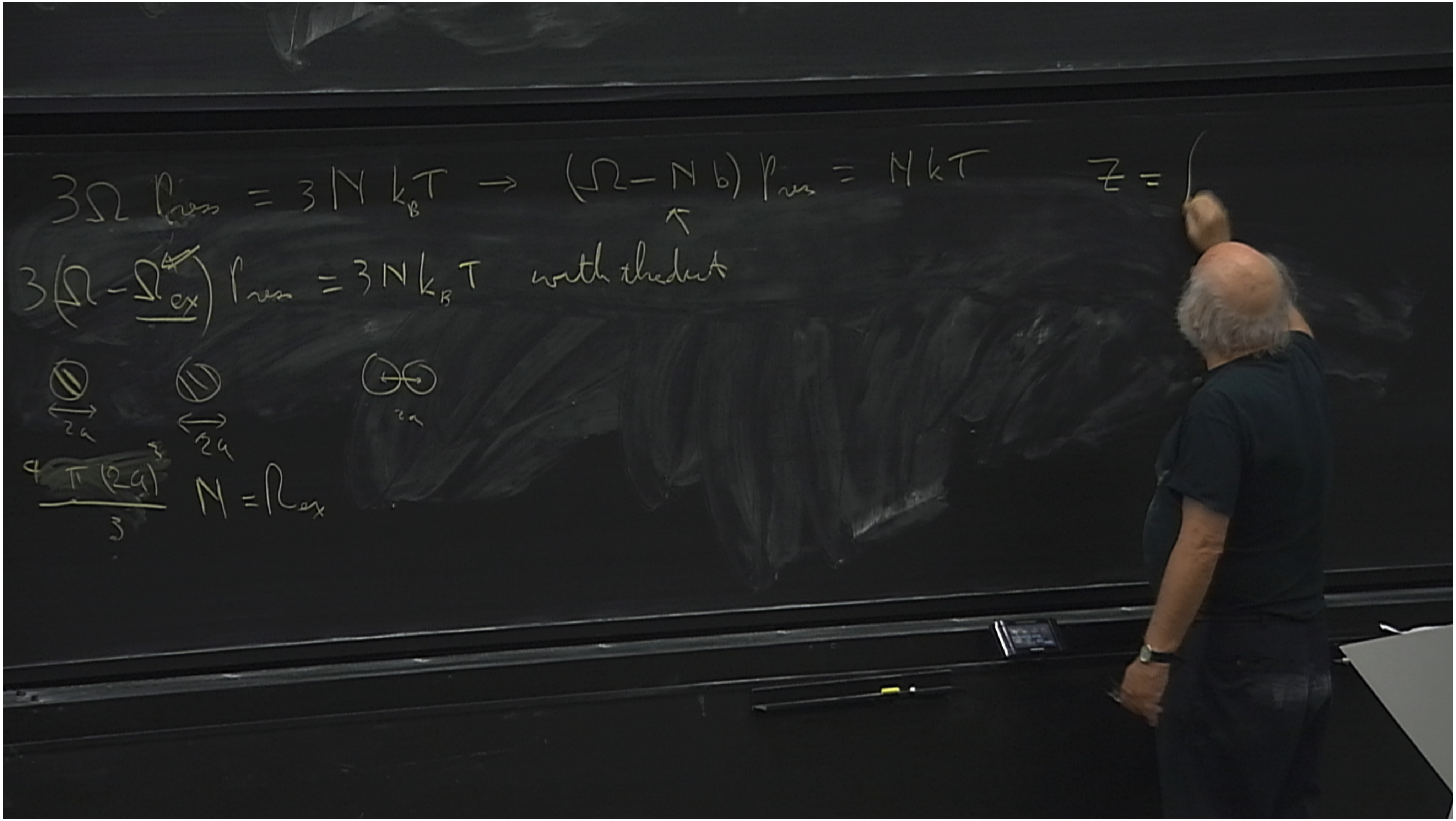
$= \sum_{\text{walls}} q_{2} P_{\text{pressure}} A \Big|_{2} + q_{1} P_{\text{pressure}} A \Big|_{1} = 3\, L\, P_{\text{pres}} A$

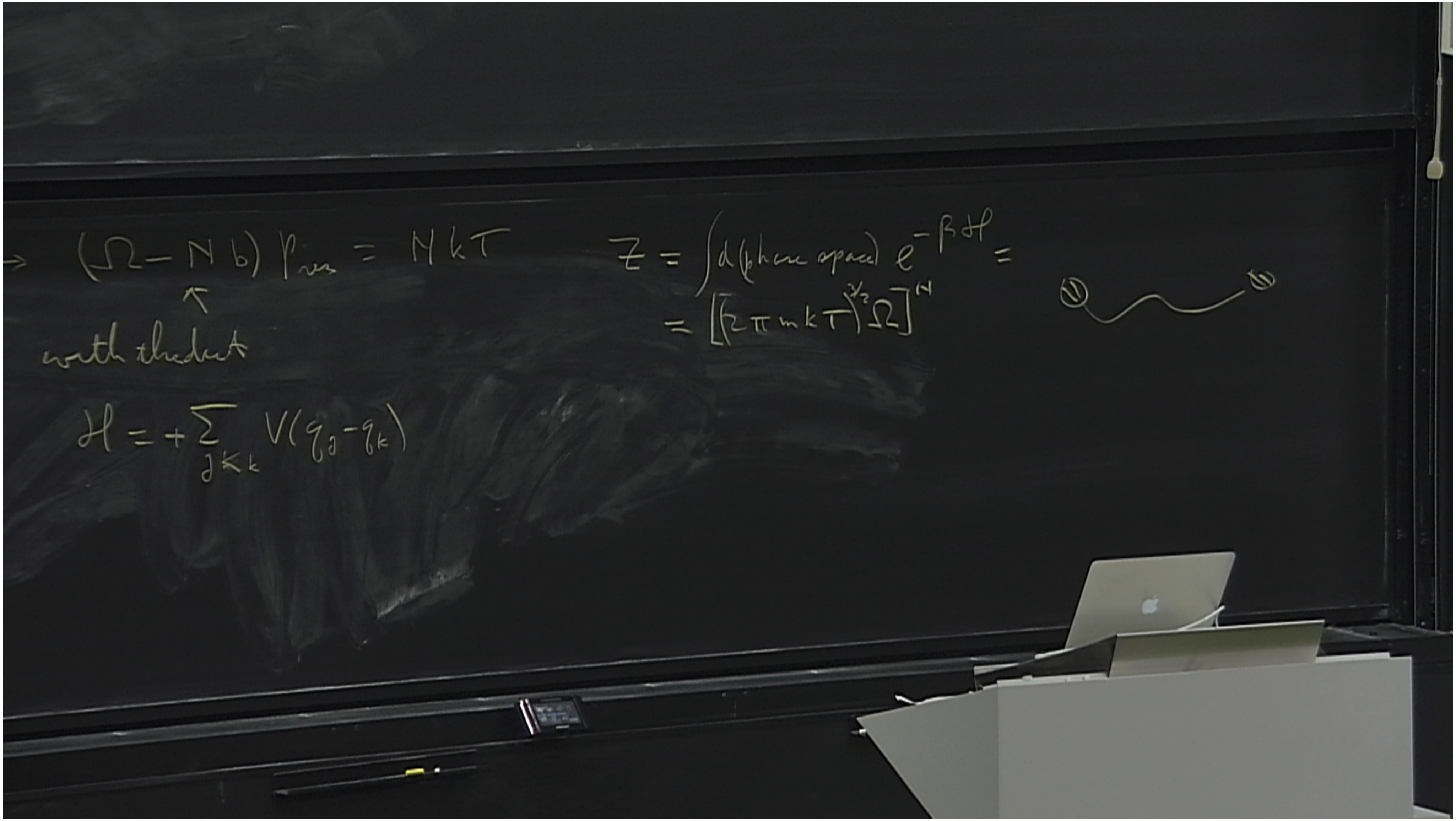



(t) − W(0) = 0
T − T_c
Q = x Q
E = ∑ p²/2m + U(q)
A
L
F
= ∑ q ∂U(q)/∂q =
= 3 L P A
Pressure
walls

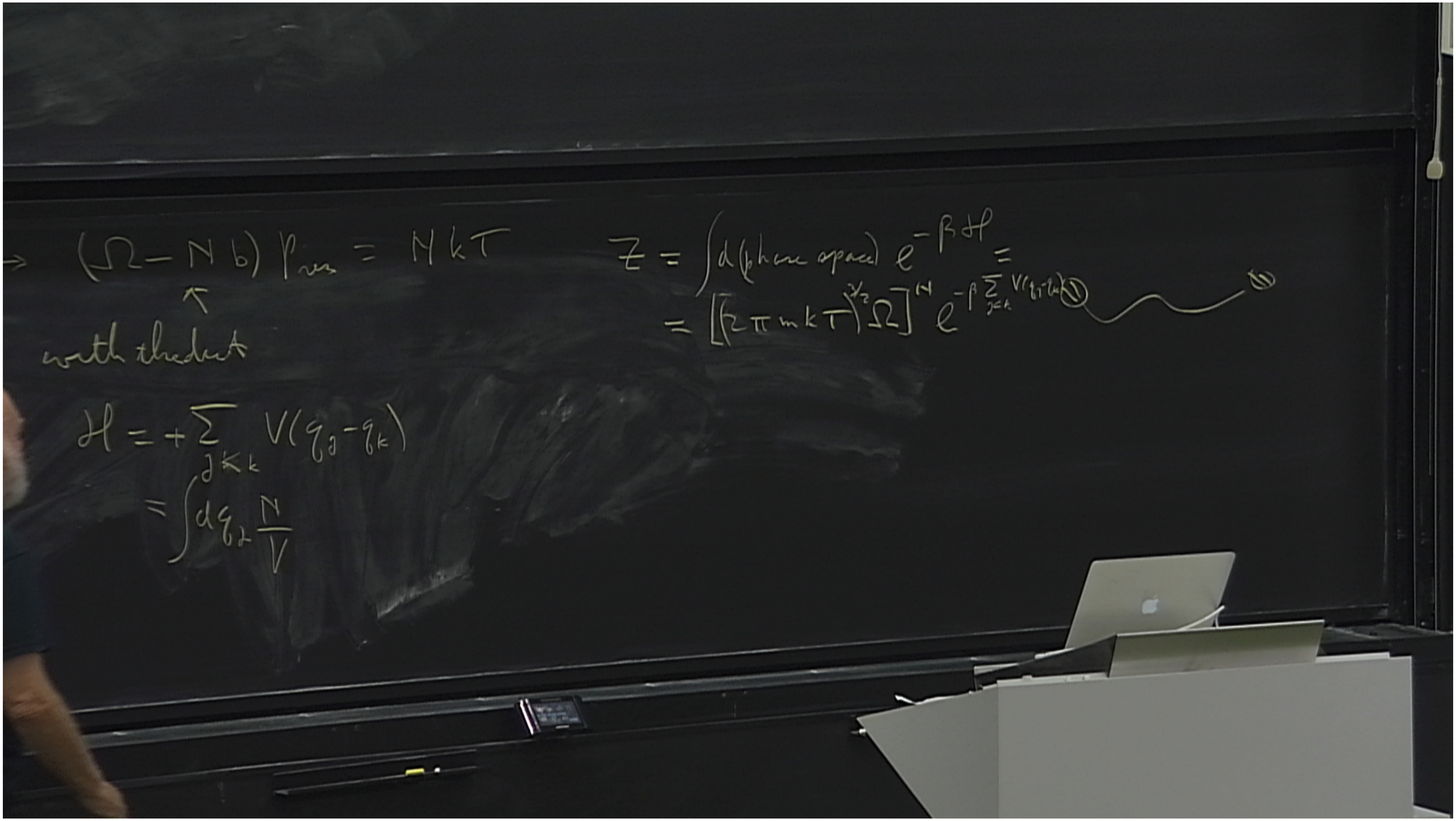


$3\Omega P_{res} = 3 N k_B T$
$3(\Omega - \Omega_{ex}) P_{res} = 3 N k_B T$ with the [illegible]

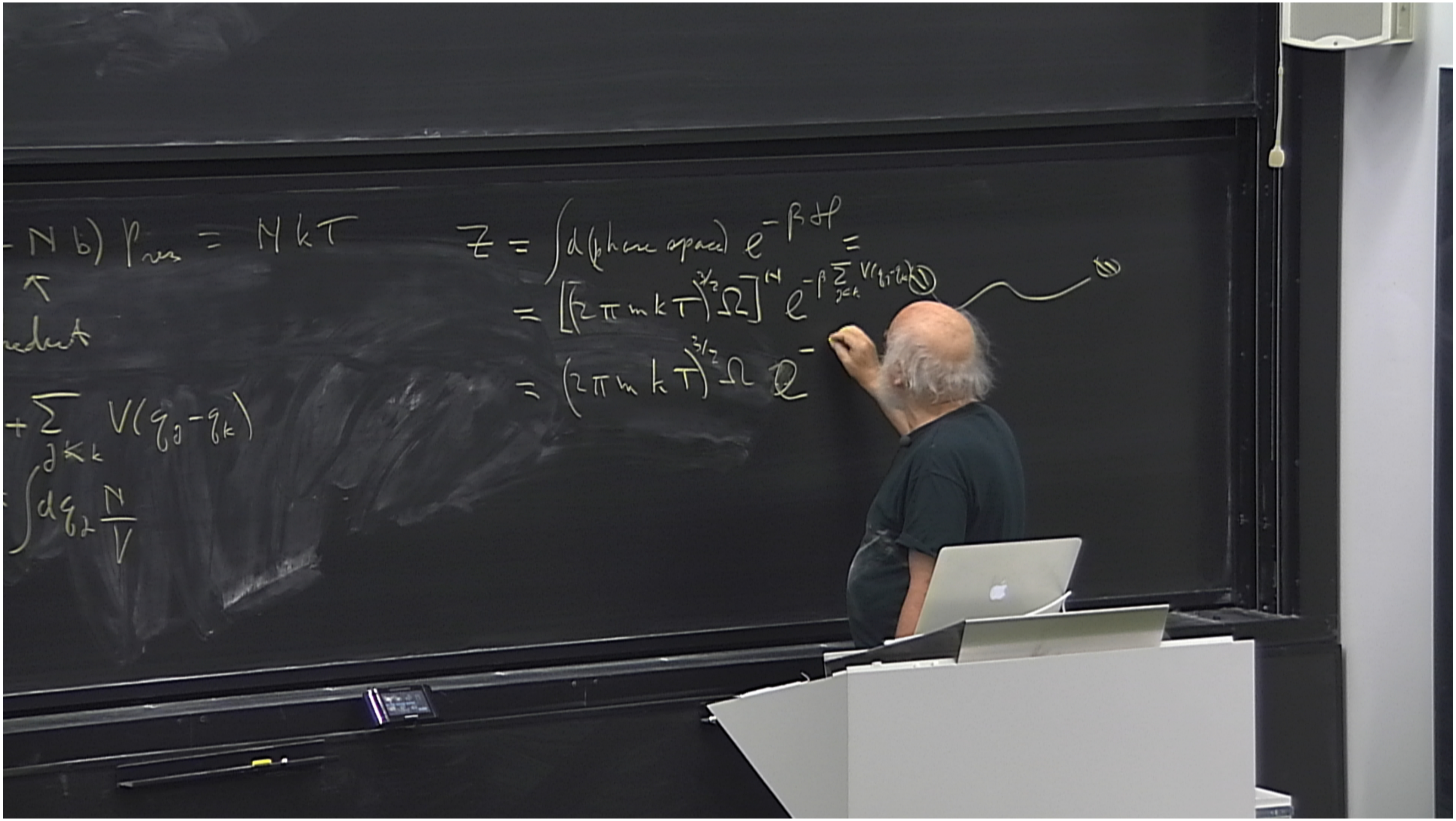

3Ω P_ves = 3 N k_B T → (Ω − N b) P_ves = N k T
Z =
3(Ω − Ω_ex) P_ves = 3 N k_B T
2a
2a
2a
4π(2a)^3 / 3 N = Ω_ex

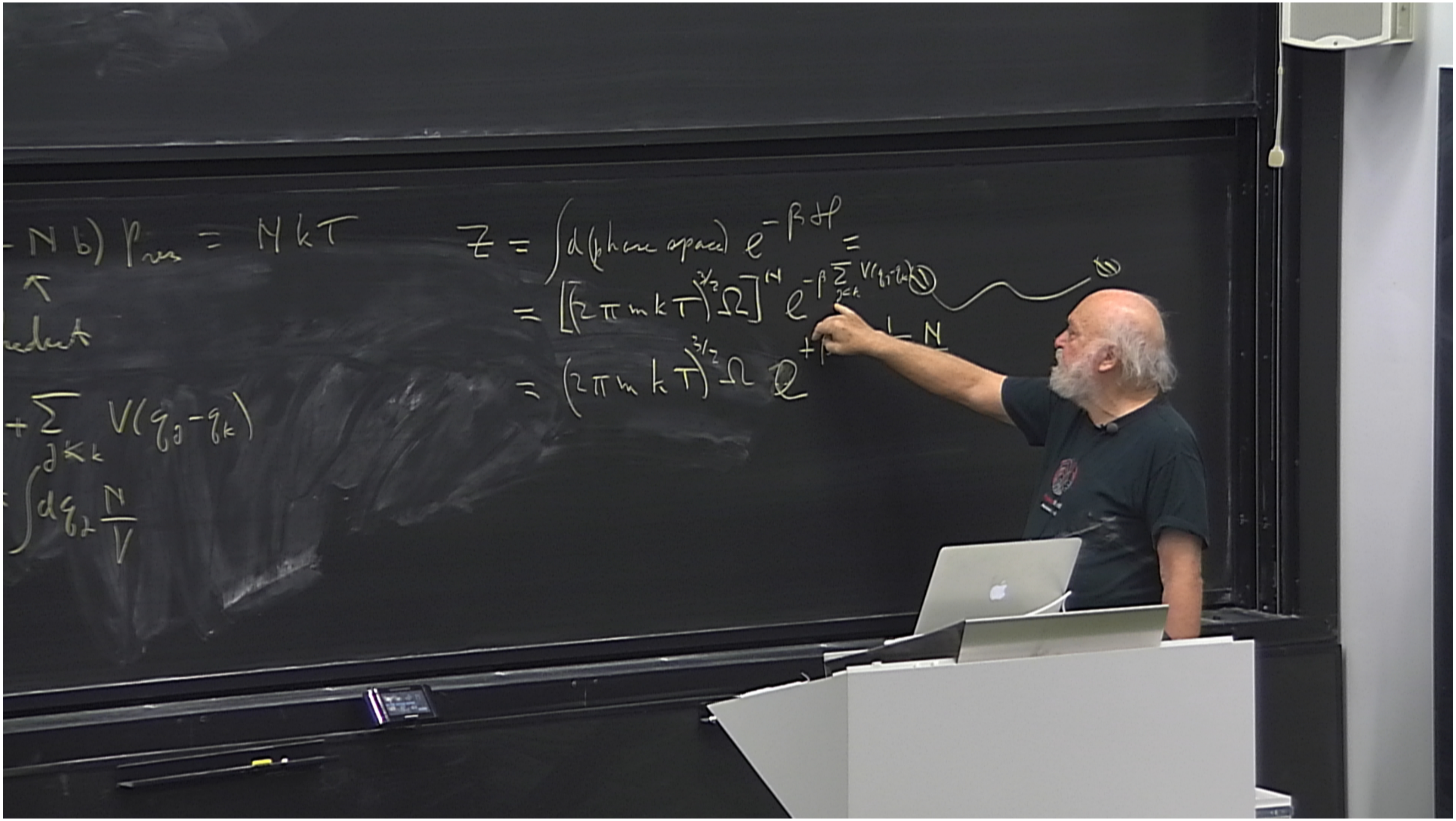


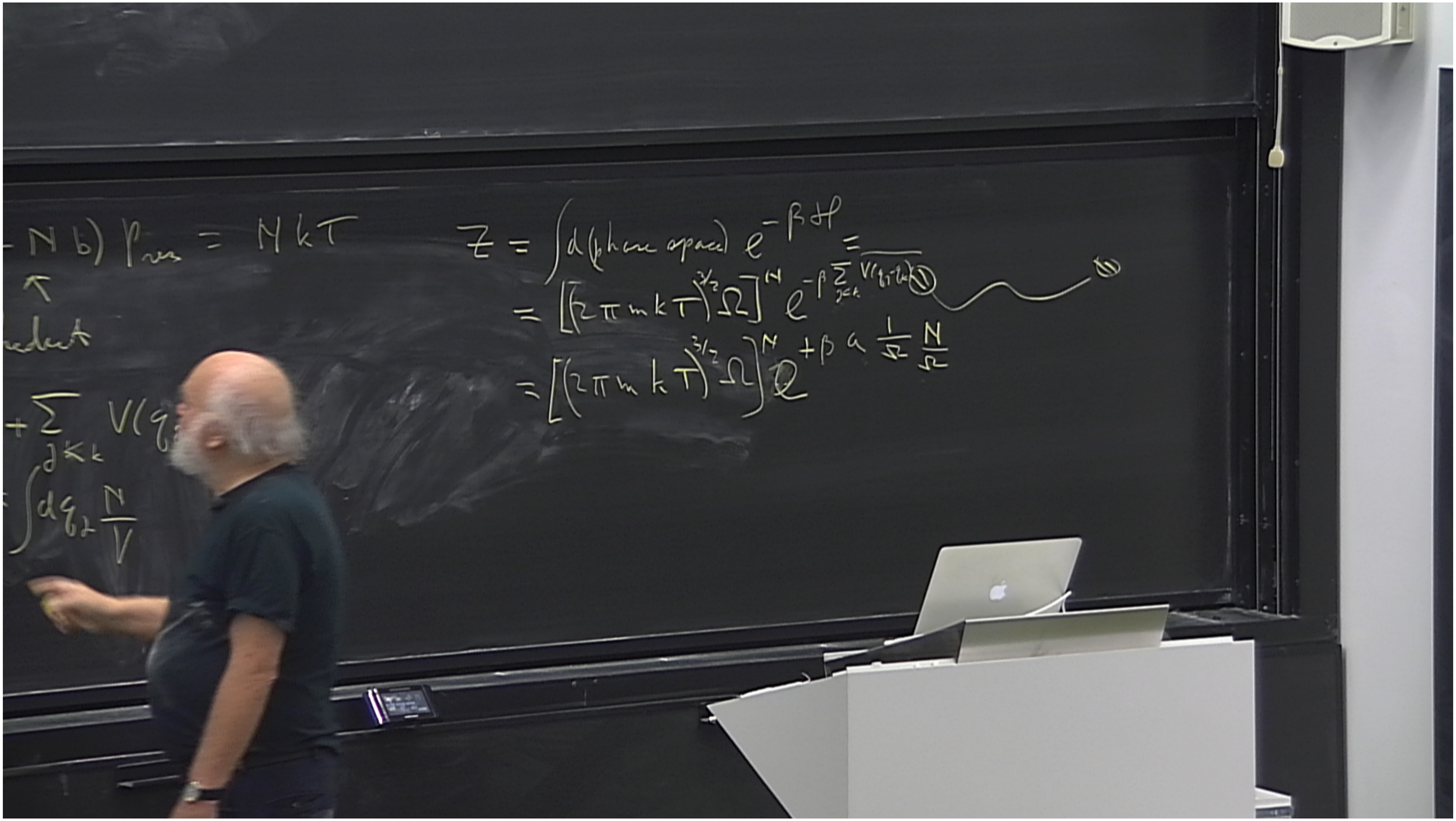
$\Rightarrow (\Omega - N b) P_{vs} = N k T$
with the
$\mathcal{H} = + \sum_{j<k} V(q_j - q_k)$
$Z = \int d(\text{phase space})\, e^{-\beta \mathcal{H}} =$
$= \left[(2\pi m k T)^{3/2} \Omega \right]^{N}$

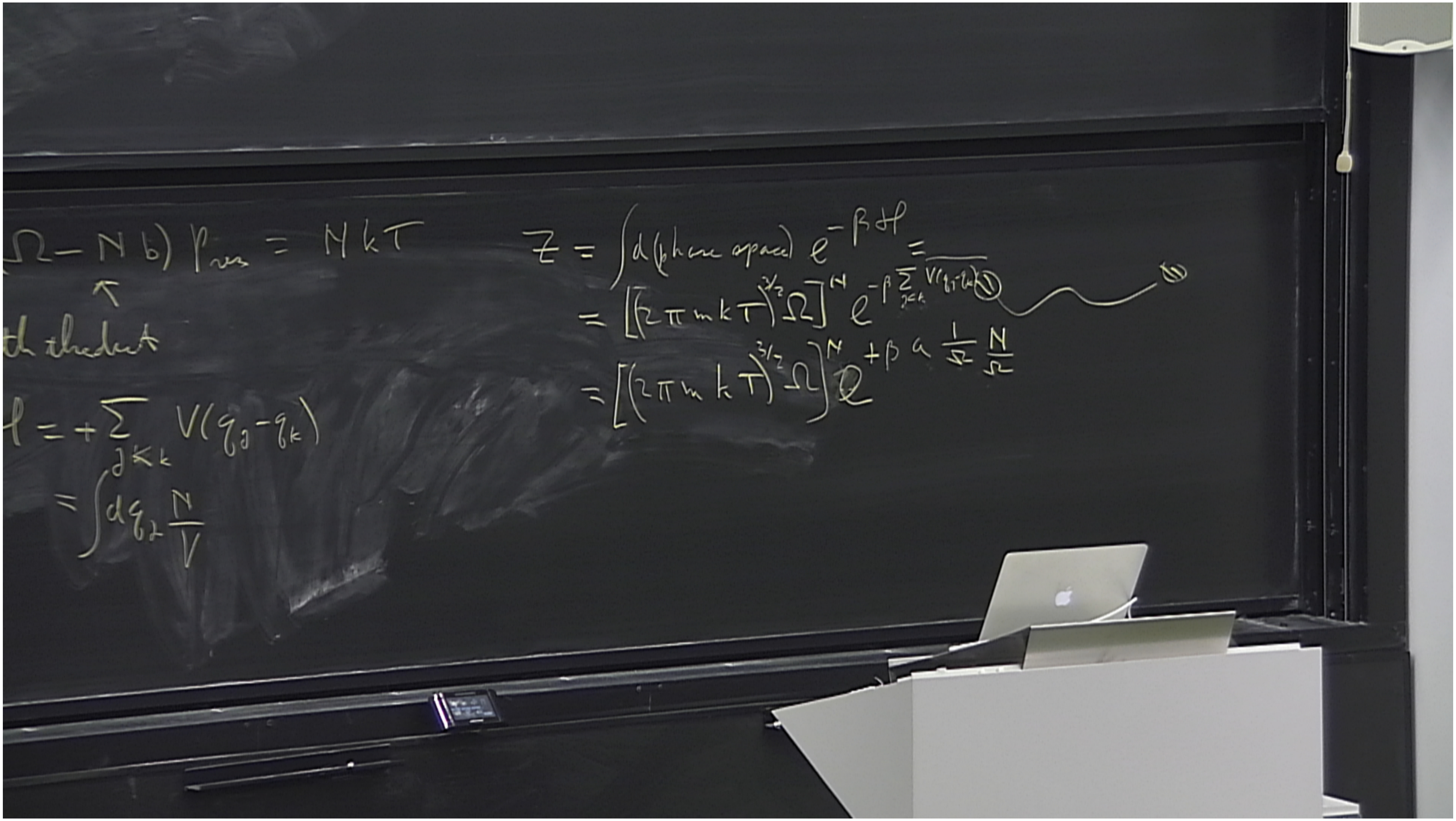

$(\Omega - N b) P = N k T$
$Z = \int d(\text{phase space})\, e^{-\beta \mathcal{H}} =$
$= [(2\pi m k T)^{3/2} \Omega]^N e^{-\beta \sum_{j<k} V(q_j - q_k)}$
$\mathcal{H} = + \sum_{j<k} V(q_j - q_k)$
$= \int d q_j \frac{N}{V}$

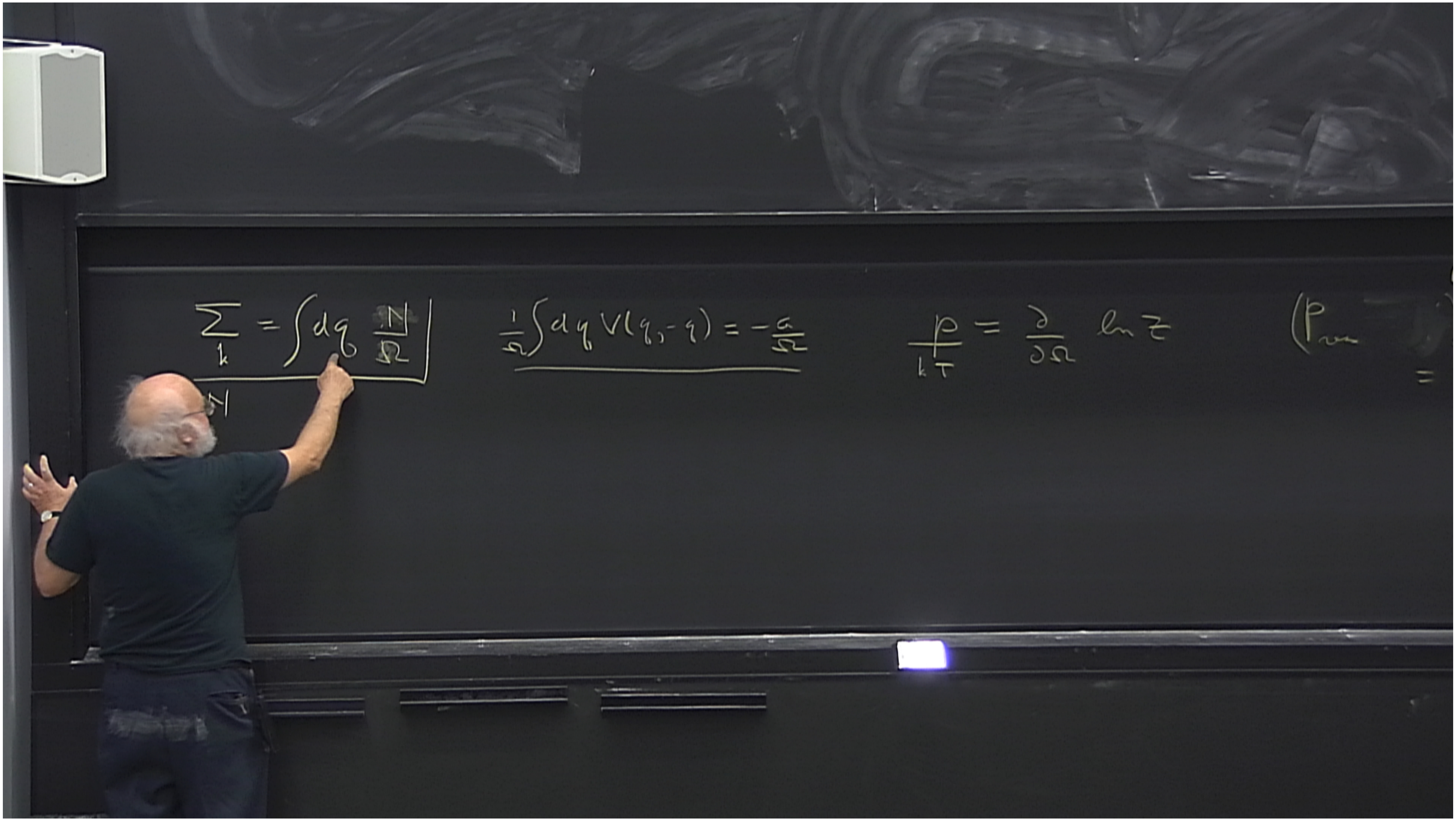
$$\sum_k = \int dq \, \frac{1}{\Omega} \qquad \frac{1}{\Omega}\int dq \, V(q, -q)$$

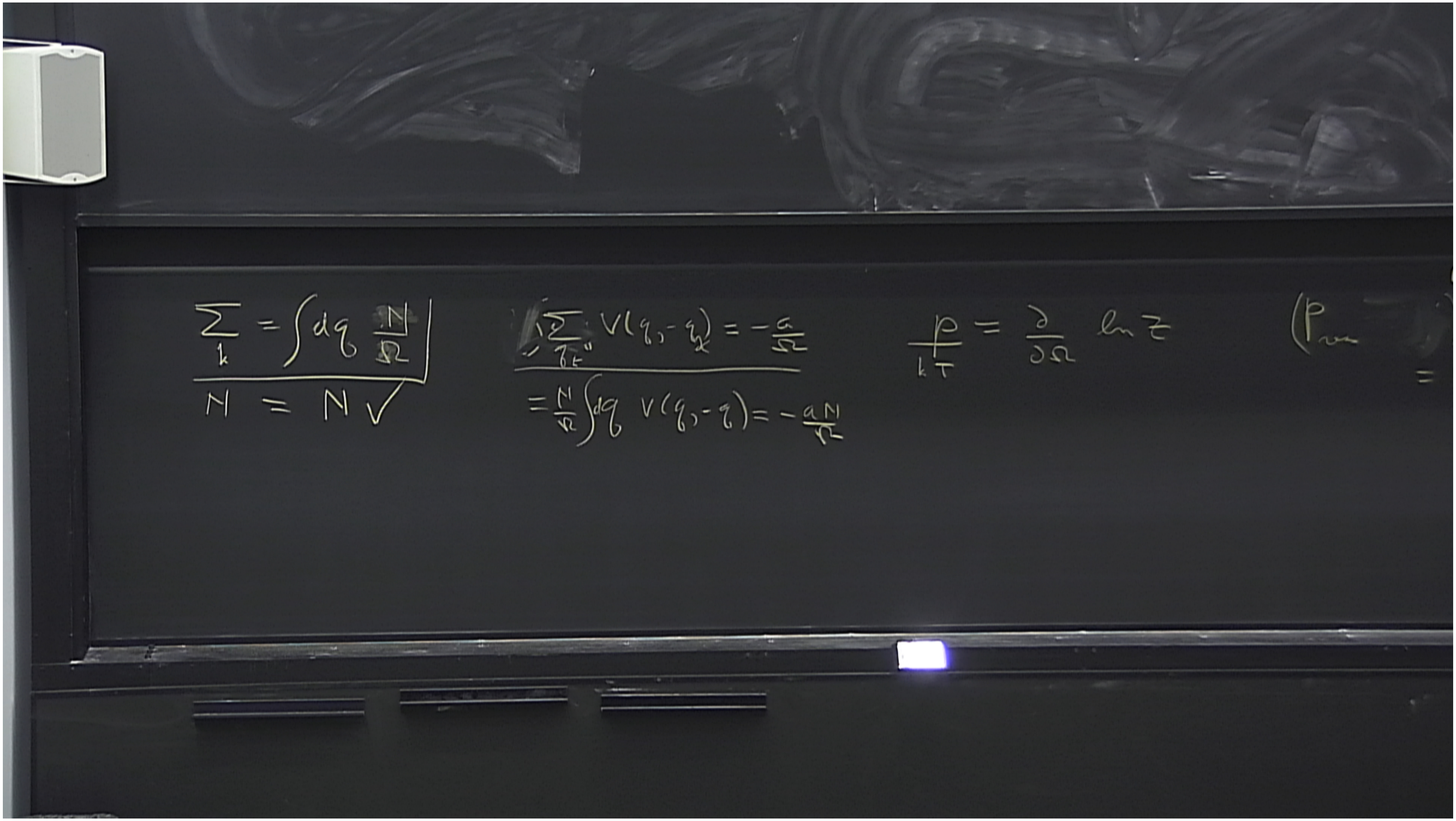

N b) P = N k T
Z = ∫ d(phase space) e^{-βH} =
= [(2π m k T)^{3/2} Ω]^N e^{-β Σ_{j<k} V(q_j - q_k)}
= (2π m k T)^{3/2} Ω e^-
+ Σ_{j<k} V(q_j - q_k)

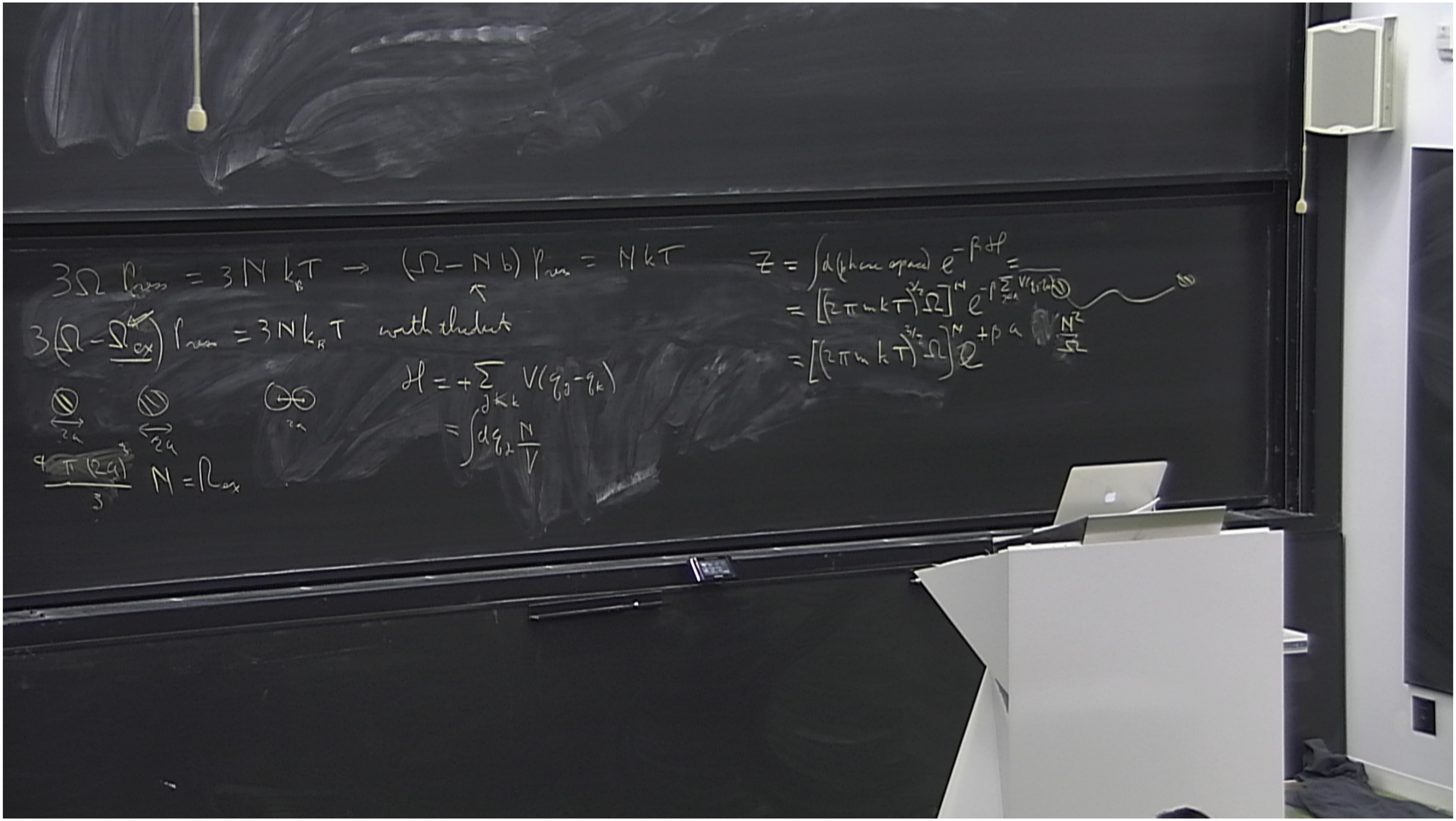

Nb) P = NkT
Z = ∫d(phase space) e^{-βH} =
= [(2πmkT)^{3/2} Ω]^N e^{-β Σ V(q_j-q_k)}
= (2πmkT)^{3/2} Ω e
+ Σ V(q_j - q_k)
j<k
∫dq_2 N/V

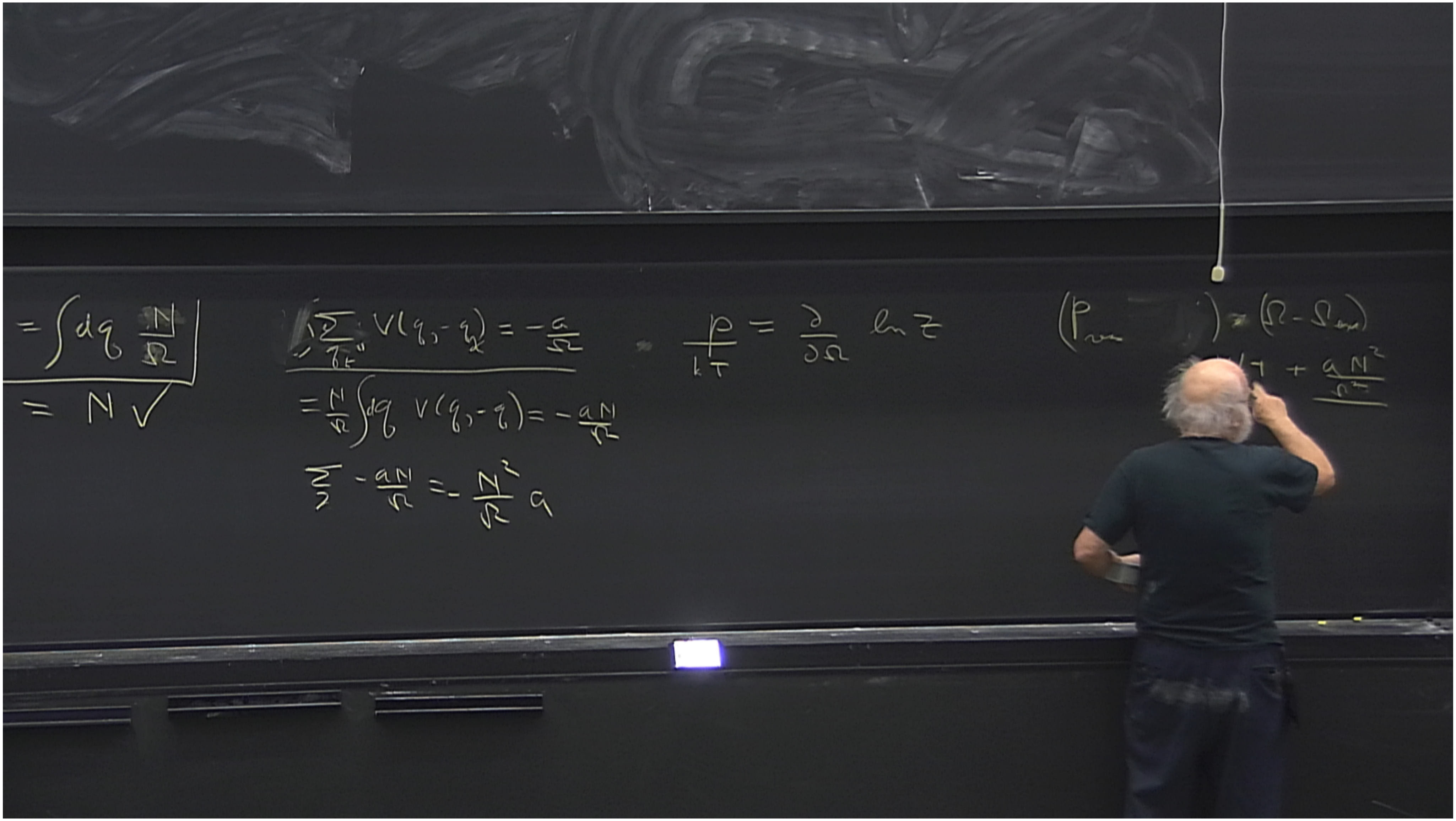

Z = ∫ d(phase space) e^{−βH} =
= [(2πmkT)^{3/2} Ω]^N e^{−β Σ V(q_j−q_k)}
= [(2πmkT)^{3/2} Ω]^N e^{+β a (1/Ω)(N/Ω)}

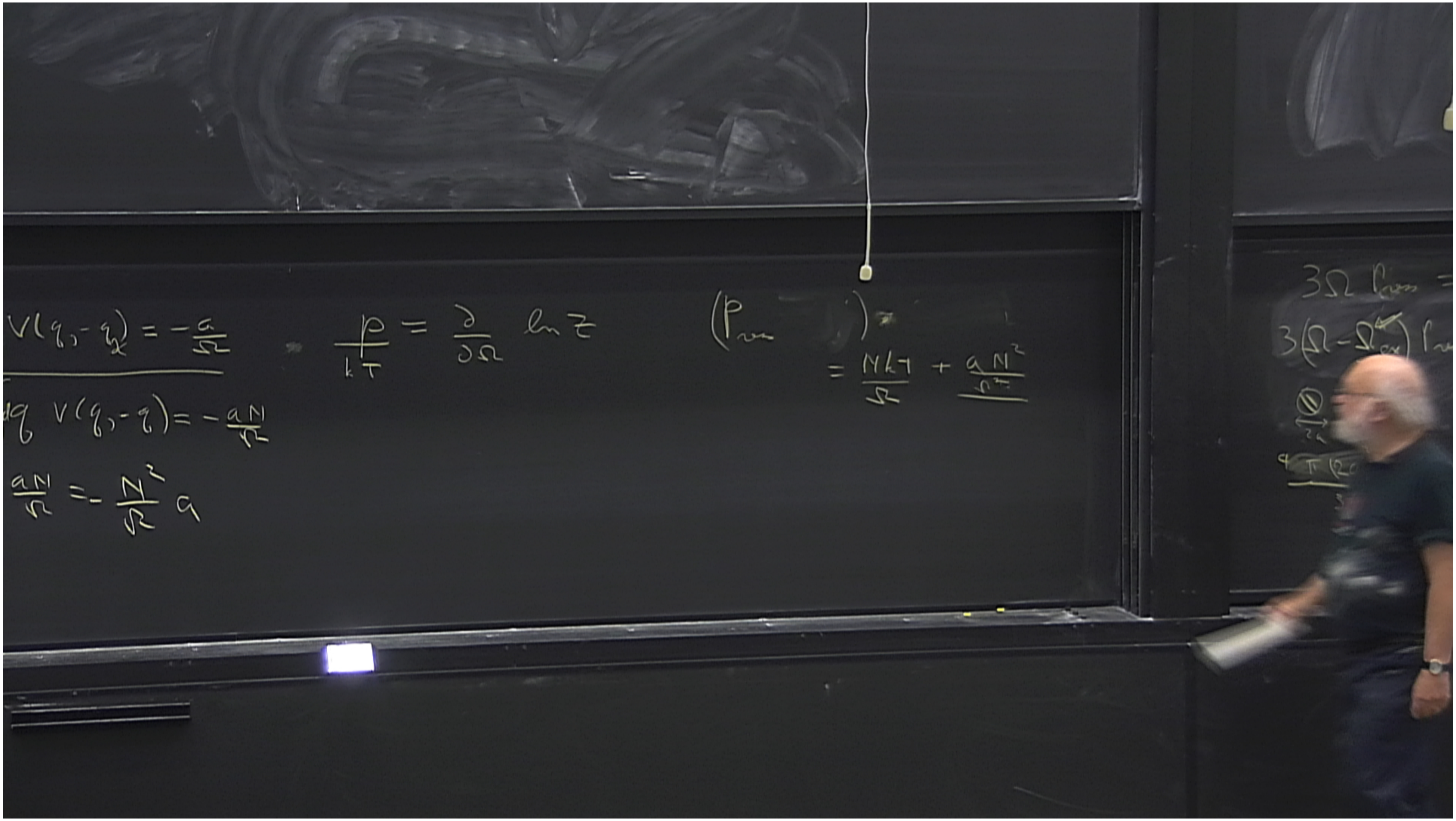

$(\Omega - Nb)\, P_{vs} = NkT$
$Z = \int d(\text{phase space})\, e^{-\beta H} =$
$= \left[(2\pi m k T)^{3/2}\Omega\right]^N e^{-\beta \sum_{j<k} V(q_j - q_k)}$
$= \left[(2\pi m k T)^{3/2}\Omega\right]^N e^{+\beta a \frac{1}{\Omega}\frac{N}{\Omega}}$
$= \left[(2\pi m k T)^{3/2}\Omega\right]^N e$
$H = +\sum_{j<k} V(q_j - q_k)$
$= \int dq_j \frac{N}{V}$

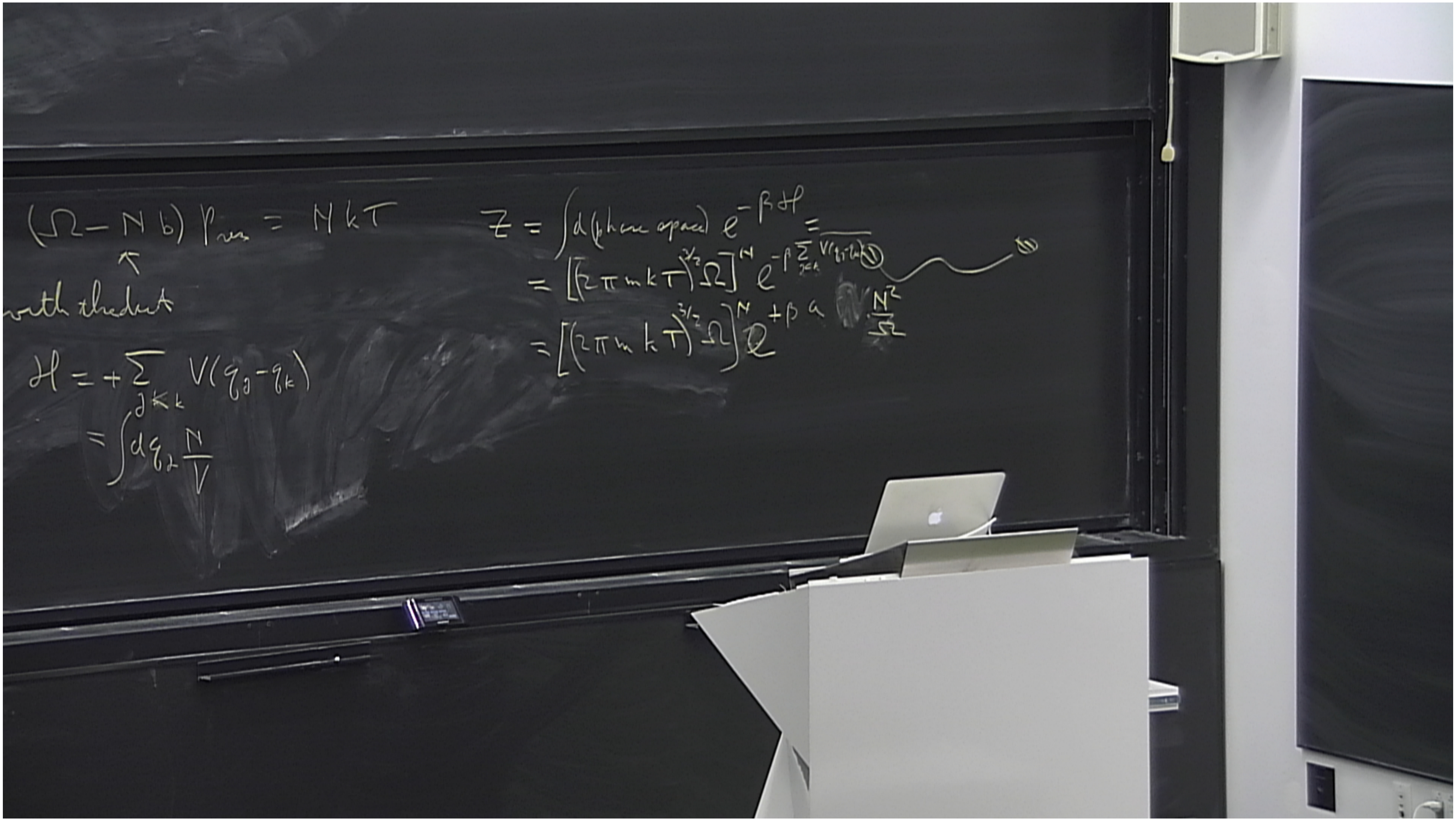

Σ_k = ∫ dq N/Ω
1/Ω ∫ dq V(q, -q) = -a/Ω
p/kT = ∂/∂Ω ln Z

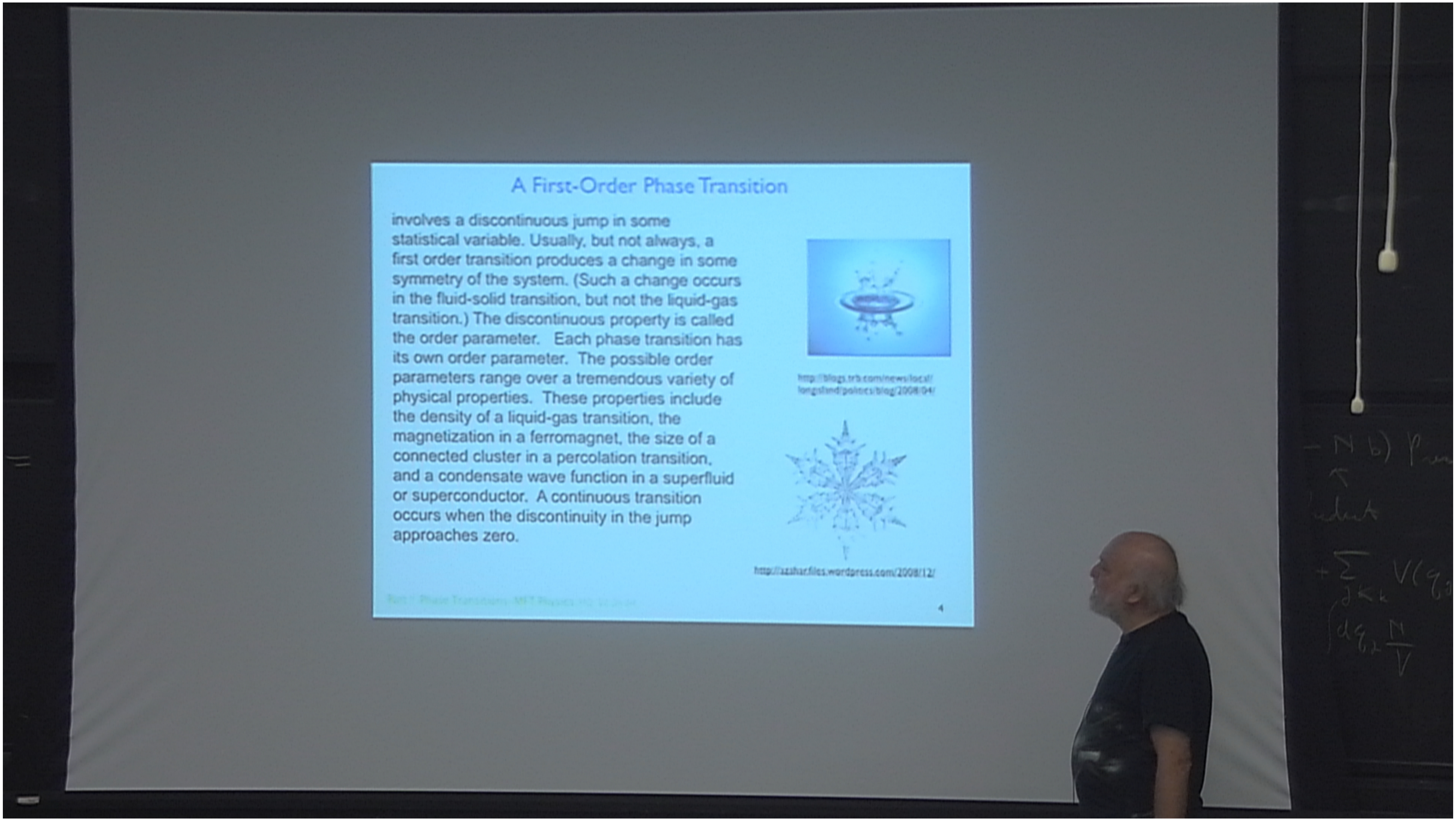

$\sum_k = \int dq \frac{N}{\Omega}$
$N = N$ ✓
$\sum V(q_i - q_j) = -\frac{a}{\Omega}$
$= \frac{N}{\Omega}\int dq\, V(q_i - q) = -\frac{aN}{\Omega}$
$\frac{p}{kT} = \frac{\partial}{\partial \Omega} \ln Z$

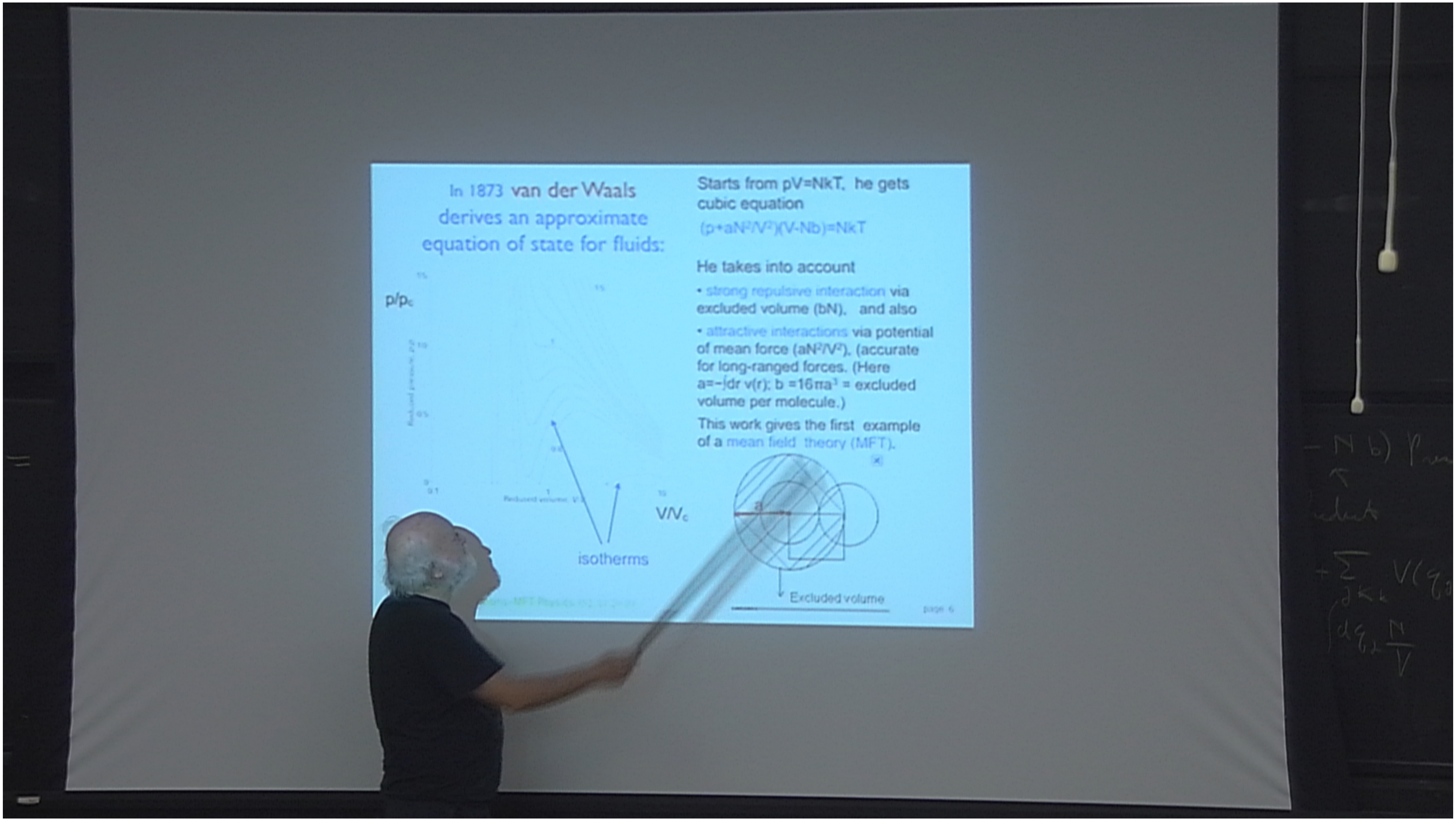

3Ω P = 3 N k_B T → (Ω − N b) P = N k T
Z = ∫ d(phase space) e^{−βH} =
H = + Σ V(q_j − q_k)
N = P_ex


= ∫dq N/Ω
= N √
V(q, -q) = -a/Ω
= N/Ω ∫dq V(q, -q) = -aN/Ω
-aN/Ω = -N²/Ω a
p/kT = ∂/∂Ω ln Z
(Ω - Ω
+ aN²/Ω²

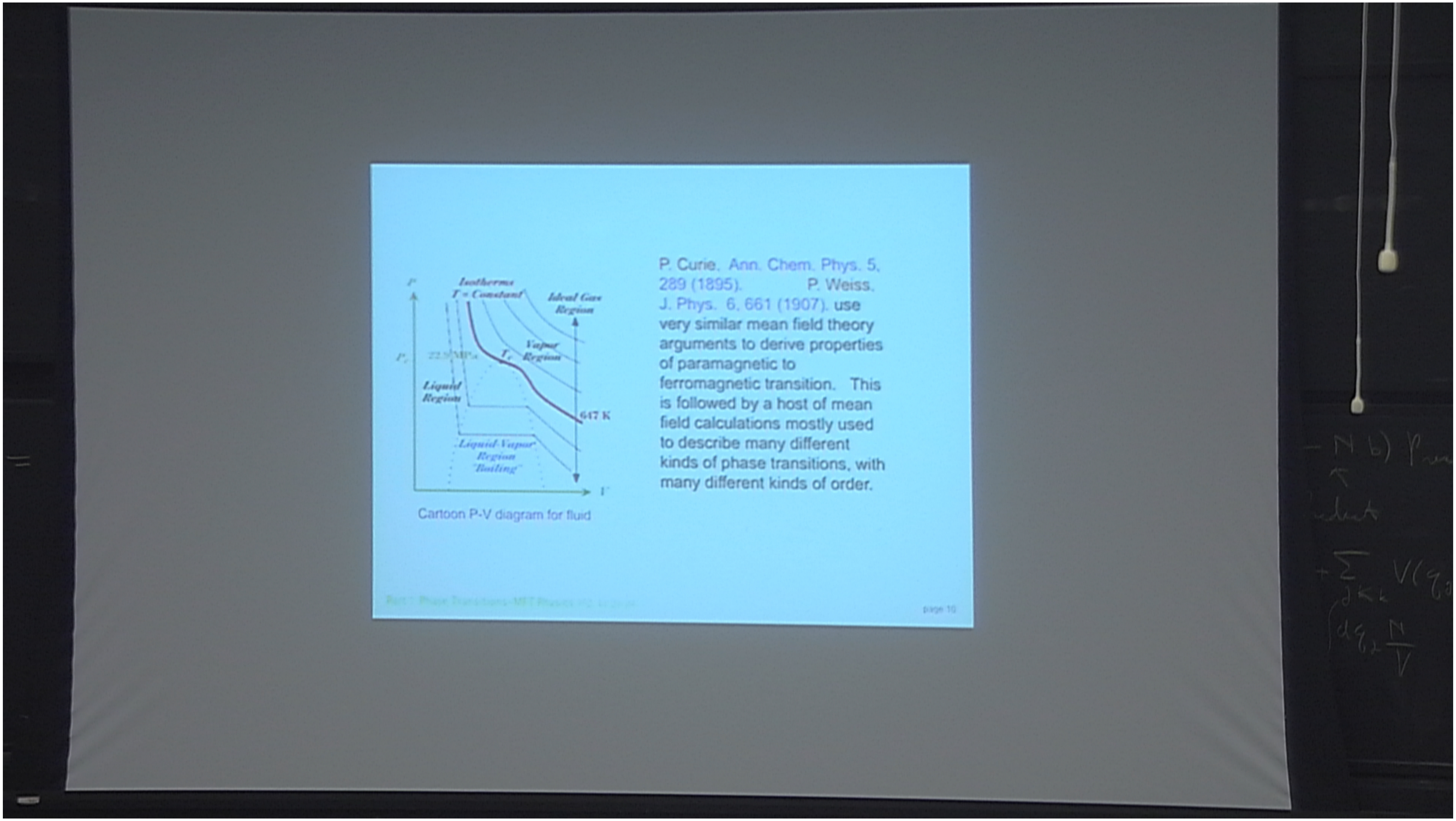

$V(q_1 - q_2) = -\frac{a}{\Omega}$
$\frac{p}{kT} = \frac{\partial}{\partial \Omega} \ln Z$
$= \frac{NkT}{\Omega} + \frac{aN^2}{\Omega^2}$
$V(q_1 - q) = -\frac{aN}{\Omega}$
$\frac{aN}{\Omega} = -\frac{N^2}{\Omega} a$


(Ω − N b) P = N k T
Z = ∫ d(phase space) e^{−βH}
= [(2πmkT)^{3/2} Ω]^N e^{−β Σ V(q_j − q_k)}
= [(2πmkT)^{3/2} Ω]^N e^{+βa N²/Ω}
H = + Σ_{j<k} V(q_j − q_k)
= ∫ dq_2 N/V


A First-Order Phase Transition
involves a discontinuous jump in some statistical variable. Usually, but not always, a first order transition produces a change in some symmetry of the system. (Such a change occurs in the fluid-solid transition, but not the liquid-gas transition.) The discontinuous property is called the order parameter. Each phase transition has its own order parameter. The possible order parameters range over a tremendous variety of physical properties. These properties include the density of a liquid-gas transition, the magnetization in a ferromagnet, the size of a connected cluster in a percolation transition, and a condensate wave function in a superfluid or superconductor. A continuous transition occurs when the discontinuity in the jump approaches zero.
4



In 1873 van der Waals derives an approximate equation of state for fluids:
p/pc
V/Vc
isotherms
Starts from pV=NkT, he gets cubic equation
(p+aN²/V²)(V-Nb)=NkT
He takes into account
• strong repulsive interaction via excluded volume (bN), and also
• attractive interactions via potential of mean force (aN²/V²). (accurate for long-ranged forces. (Here a=−∫dr v(r); b =16πa³ = excluded volume per molecule.)
This work gives the first example of a mean field theory (MFT).
a
Excluded volume


Isotherms
T = Constant
Ideal Gas
Region
Vapor
Region
Liquid
Region
647 K
Liquid-Vapor
Region
"Boiling"
Cartoon P-V diagram for fluid
P. Curie. Ann. Chem. Phys. 5, 289 (1895). P. Weiss. J. Phys. 6, 661 (1907). use very similar mean field theory arguments to derive properties of paramagnetic to ferromagnetic transition. This is followed by a host of mean field calculations mostly used to describe many different kinds of phase transitions, with many different kinds of order.
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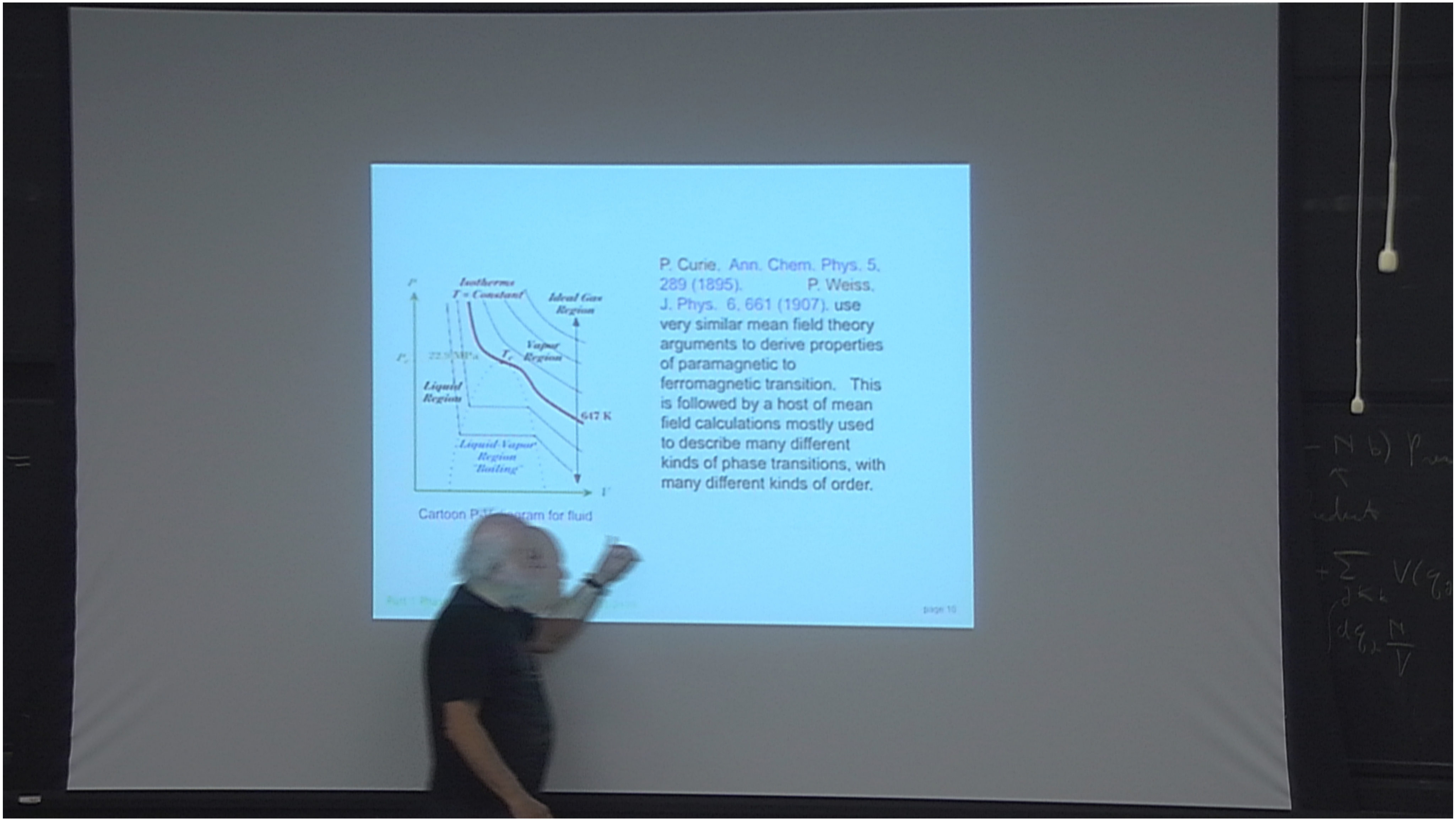
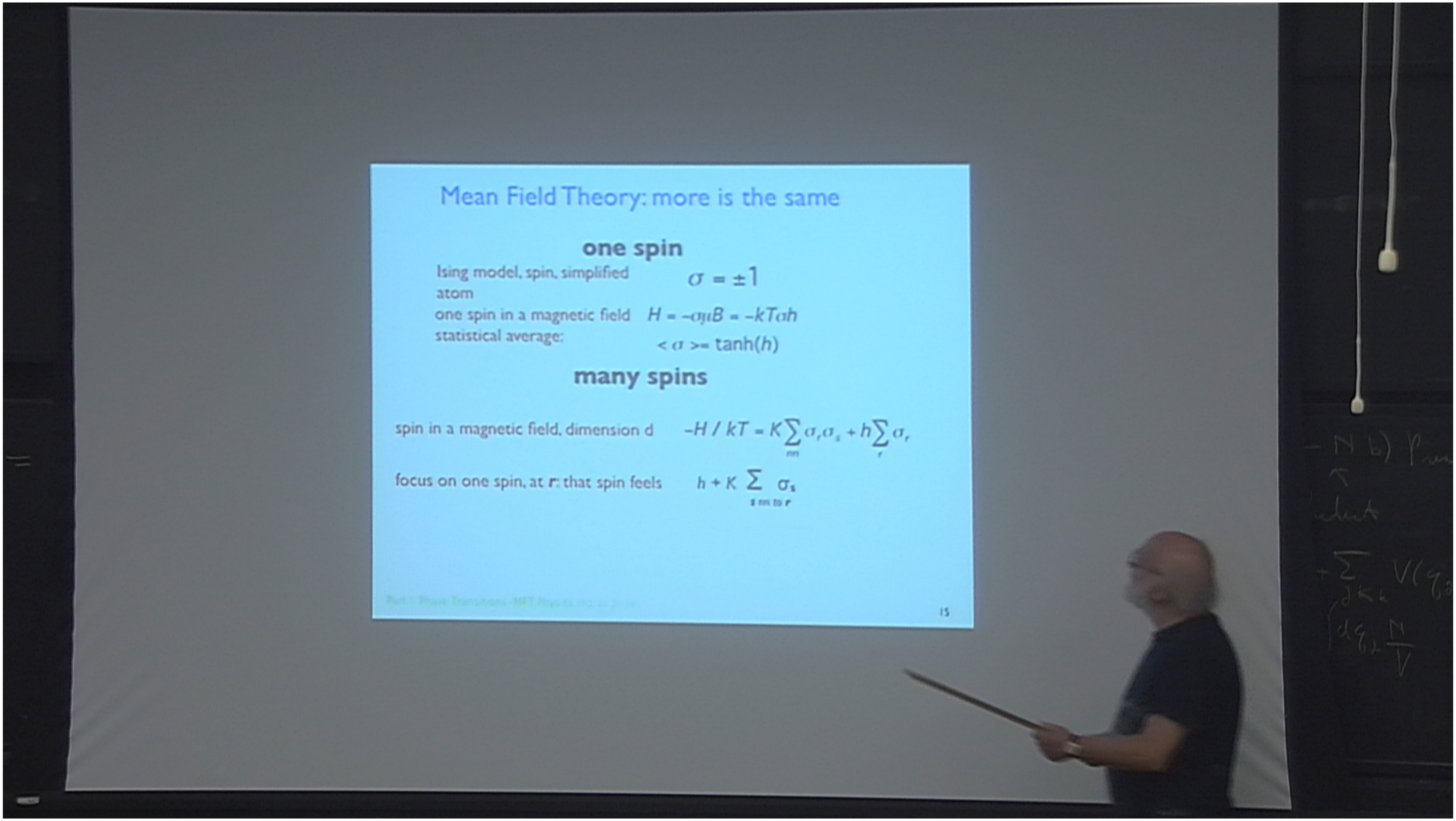

Isotherms
T = Constant
Ideal Gas Region
Vapor Region
22.9 MPa
Liquid Region
647 K
Liquid-Vapor Region "Boiling"
Cartoon P
gram for fluid
P. Curie. Ann. Chem. Phys. 5, 289 (1895). P. Weiss. J. Phys. 6, 661 (1907). use very similar mean field theory arguments to derive properties of paramagnetic to ferromagnetic transition. This is followed by a host of mean field calculations mostly used to describe many different kinds of phase transitions, with many different kinds of order.


Mean Field Theory: more is the same
one spin
Ising model, spin, simplified atom
$\sigma = \pm 1$
one spin in a magnetic field
$H = -\sigma\mu B = -kT\sigma h$
statistical average:
$<\sigma>= \tanh(h)$
many spins
spin in a magnetic field, dimension d
$-H/kT = K\sum_{nn}\sigma_r\sigma_s + h\sum_r \sigma_r$
focus on one spin, at r: that spin feels
$h + K \sum_{s \text{ nn to } r} \sigma_s$
15

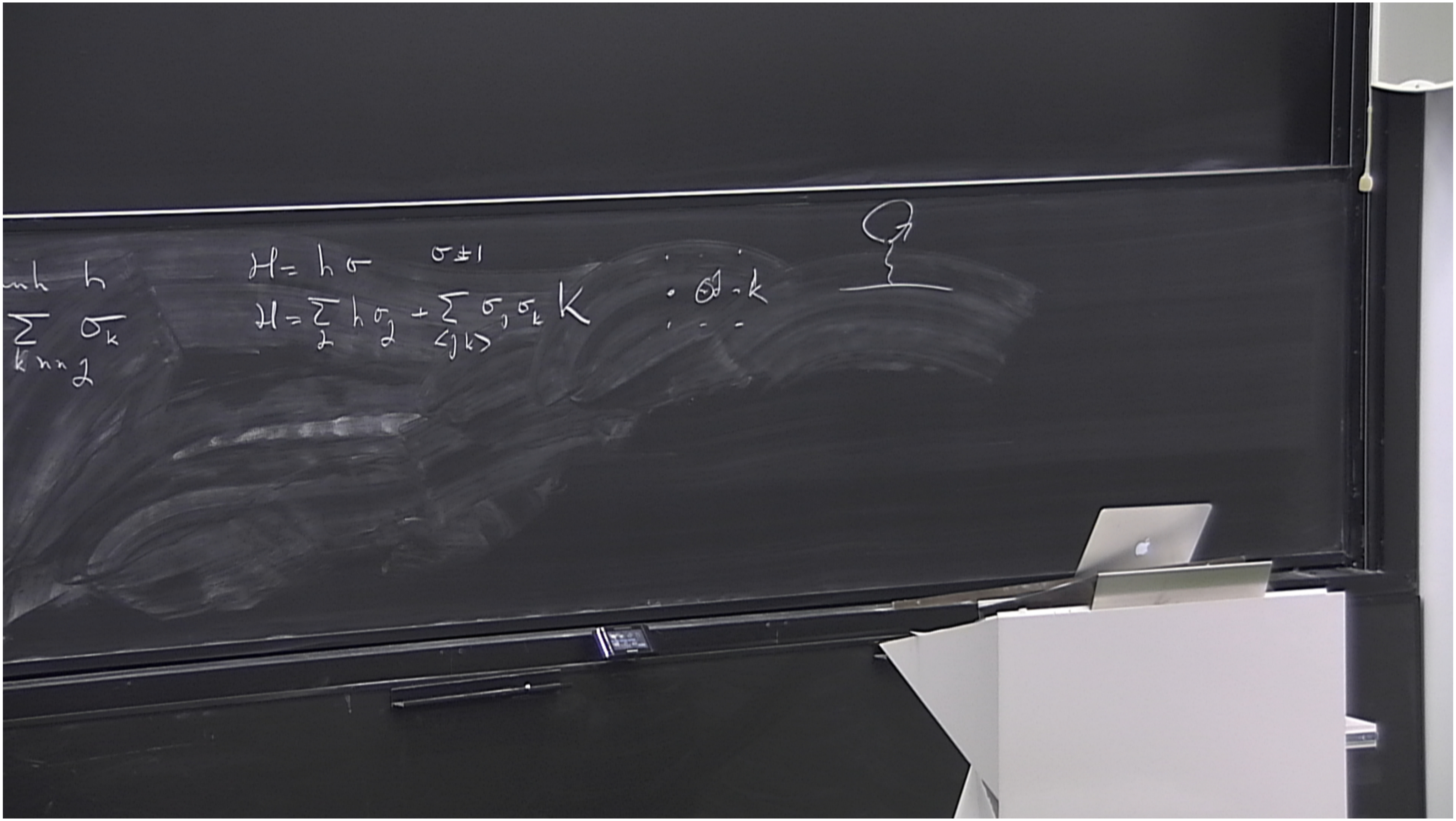
$$\langle \sigma \rangle = \tanh h$$

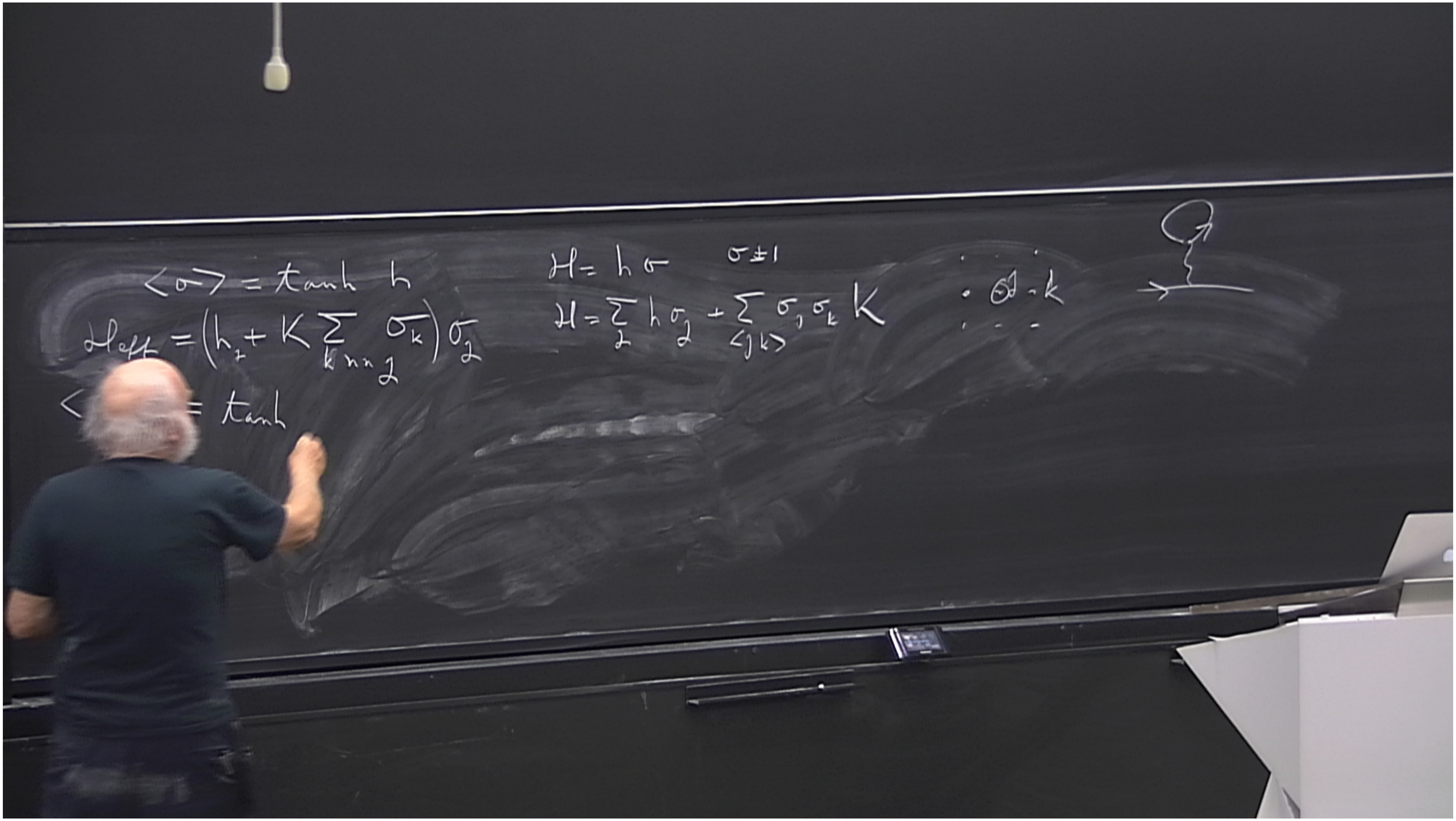
$$H_{eff} = h + K \sum_{k\,nn\,j} \sigma_k$$

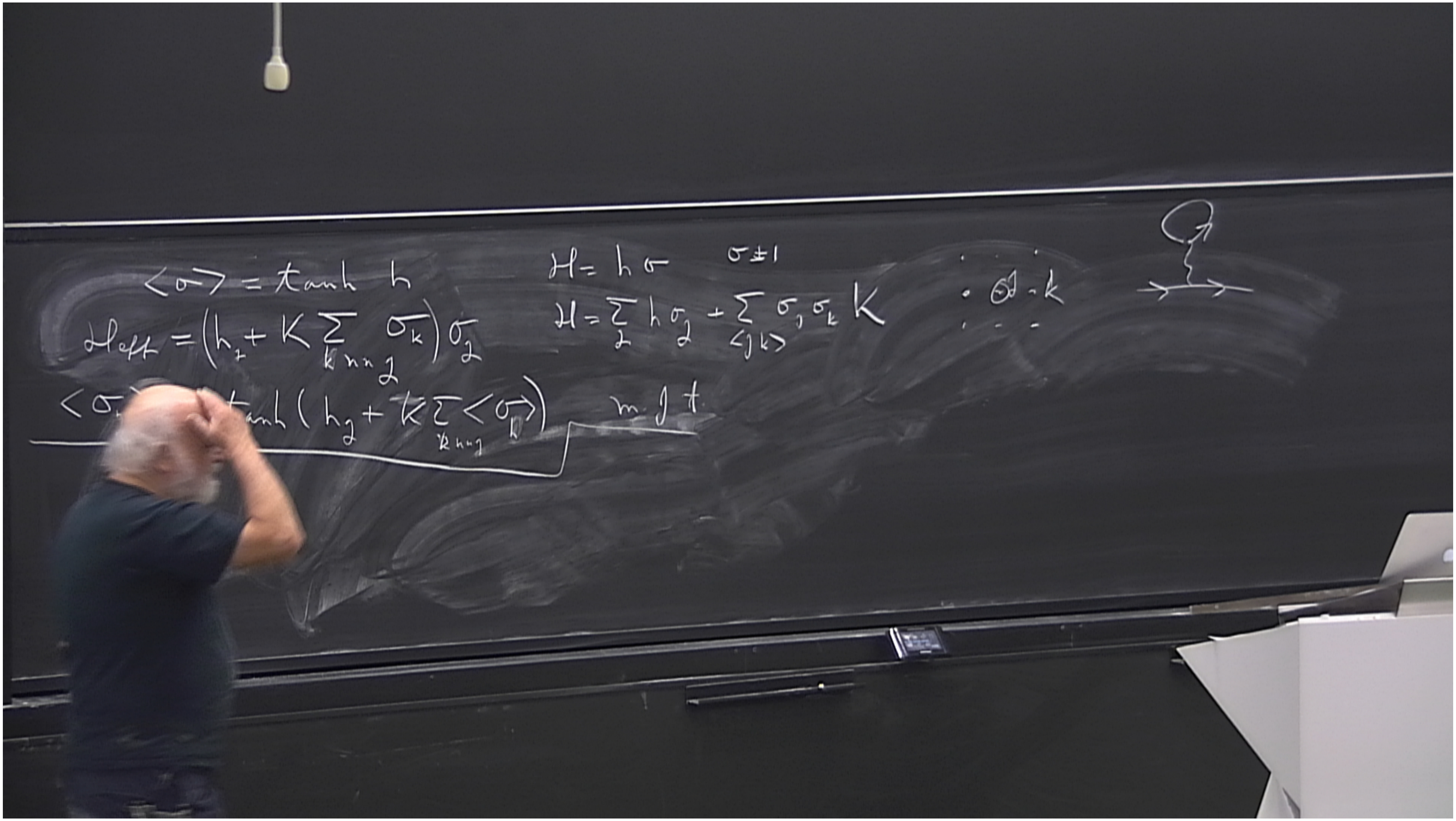
$$H = h\sigma \qquad \sigma = \pm 1$$

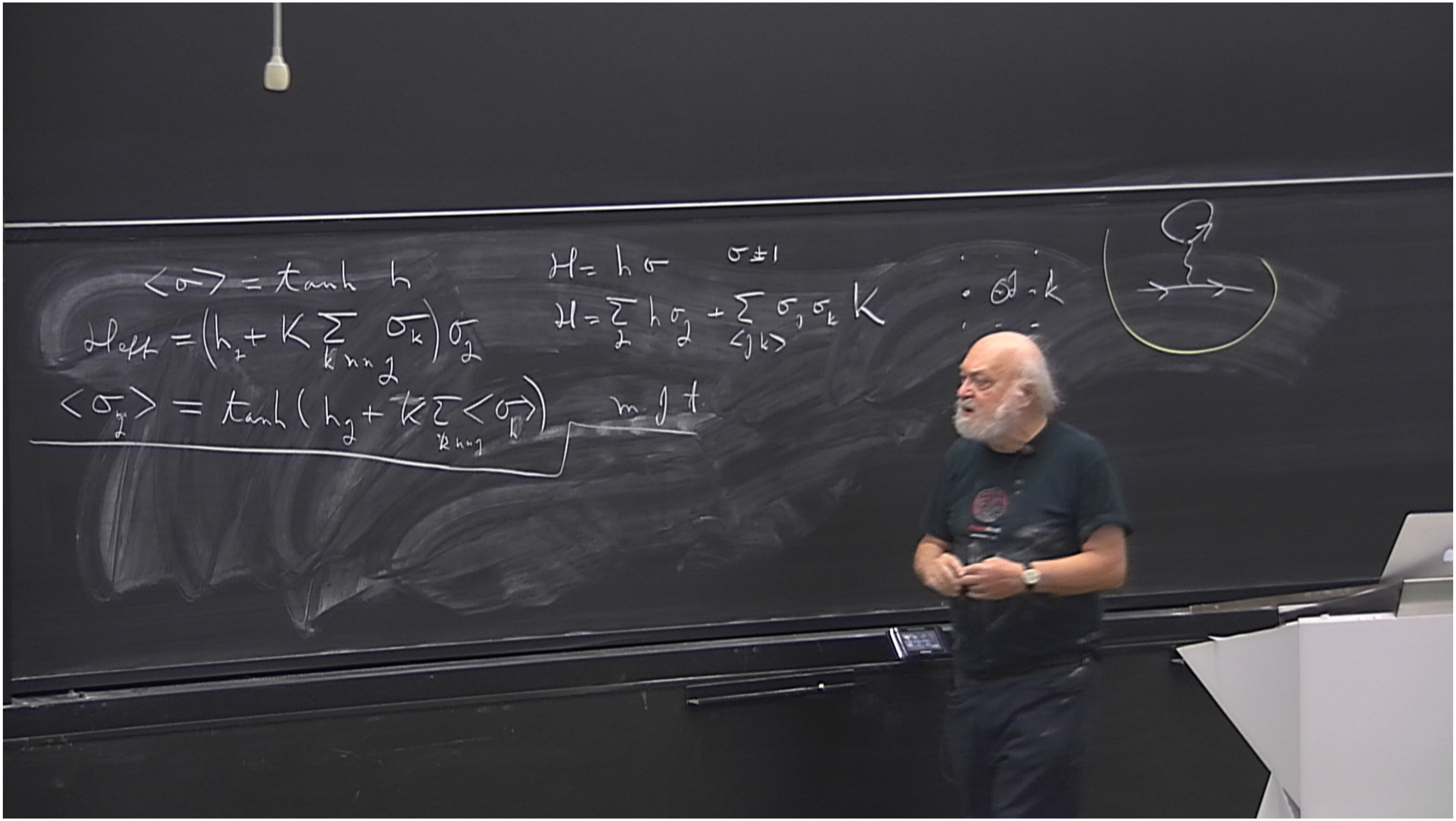
$$H = \sum_j h \sigma_j + \sum_{\langle jk \rangle} \sigma_j \sigma_k K$$

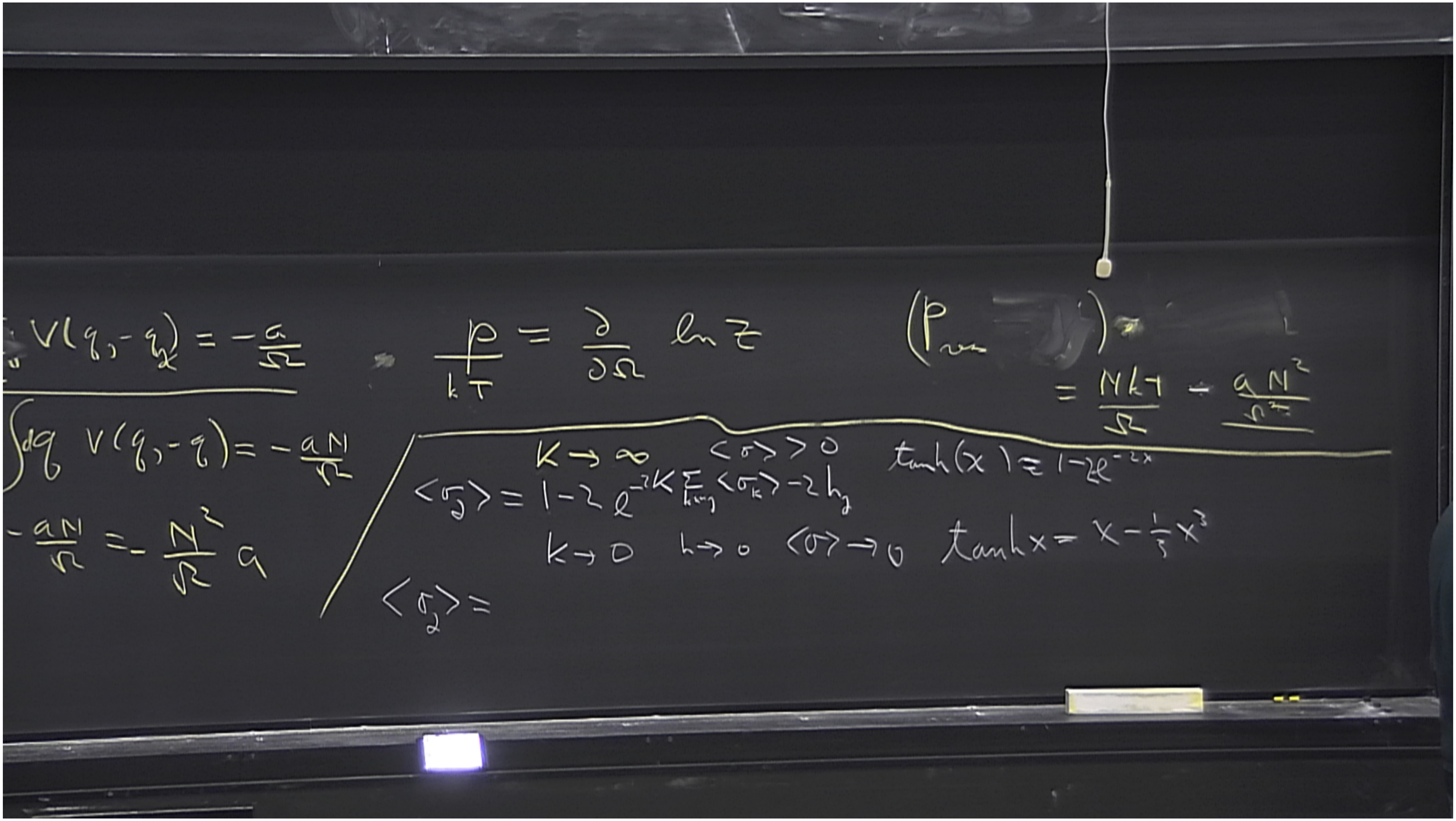
$j - k$

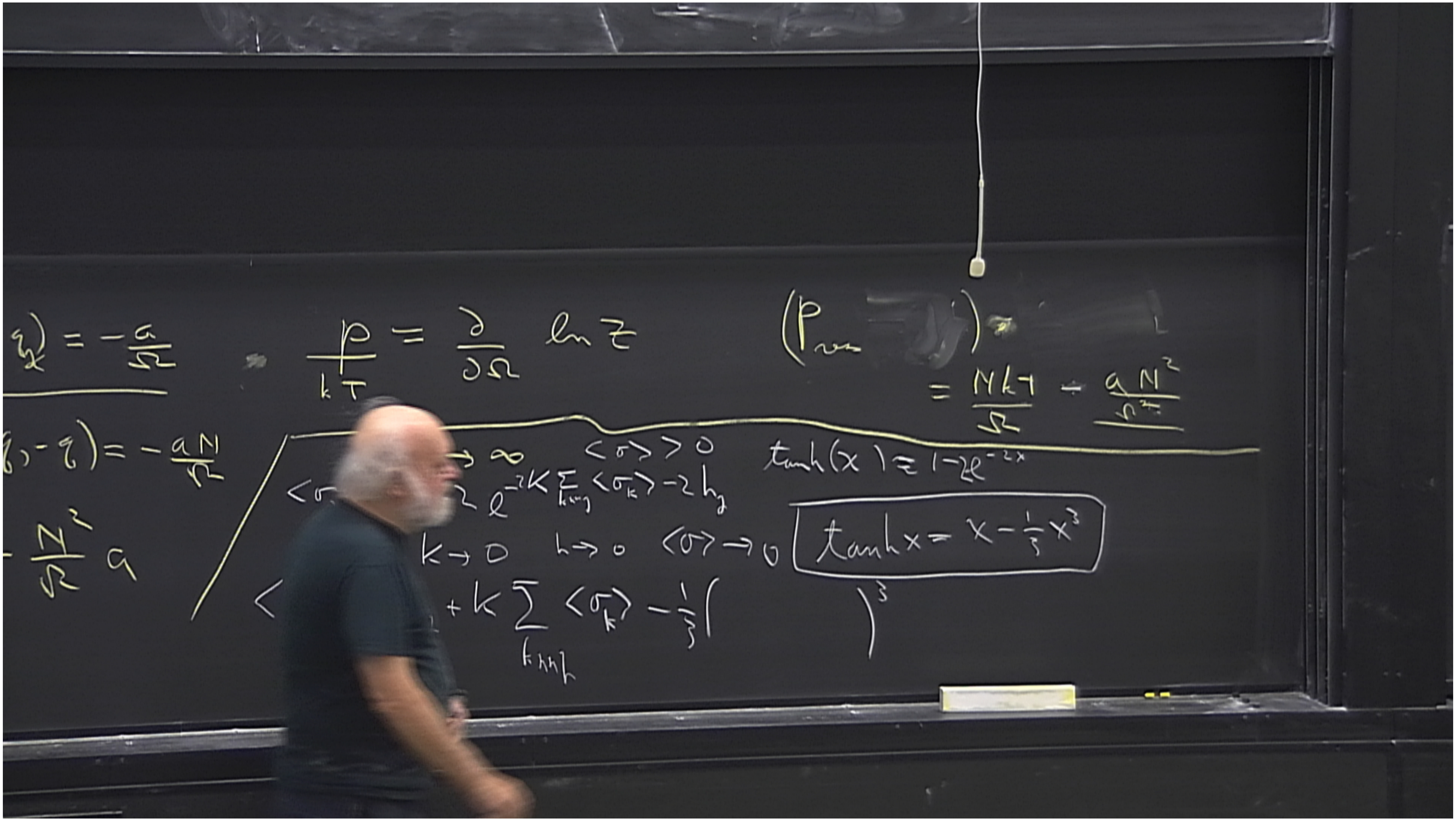

H = h σ
σ ±1
H = Σ h σ + Σ σ σ K

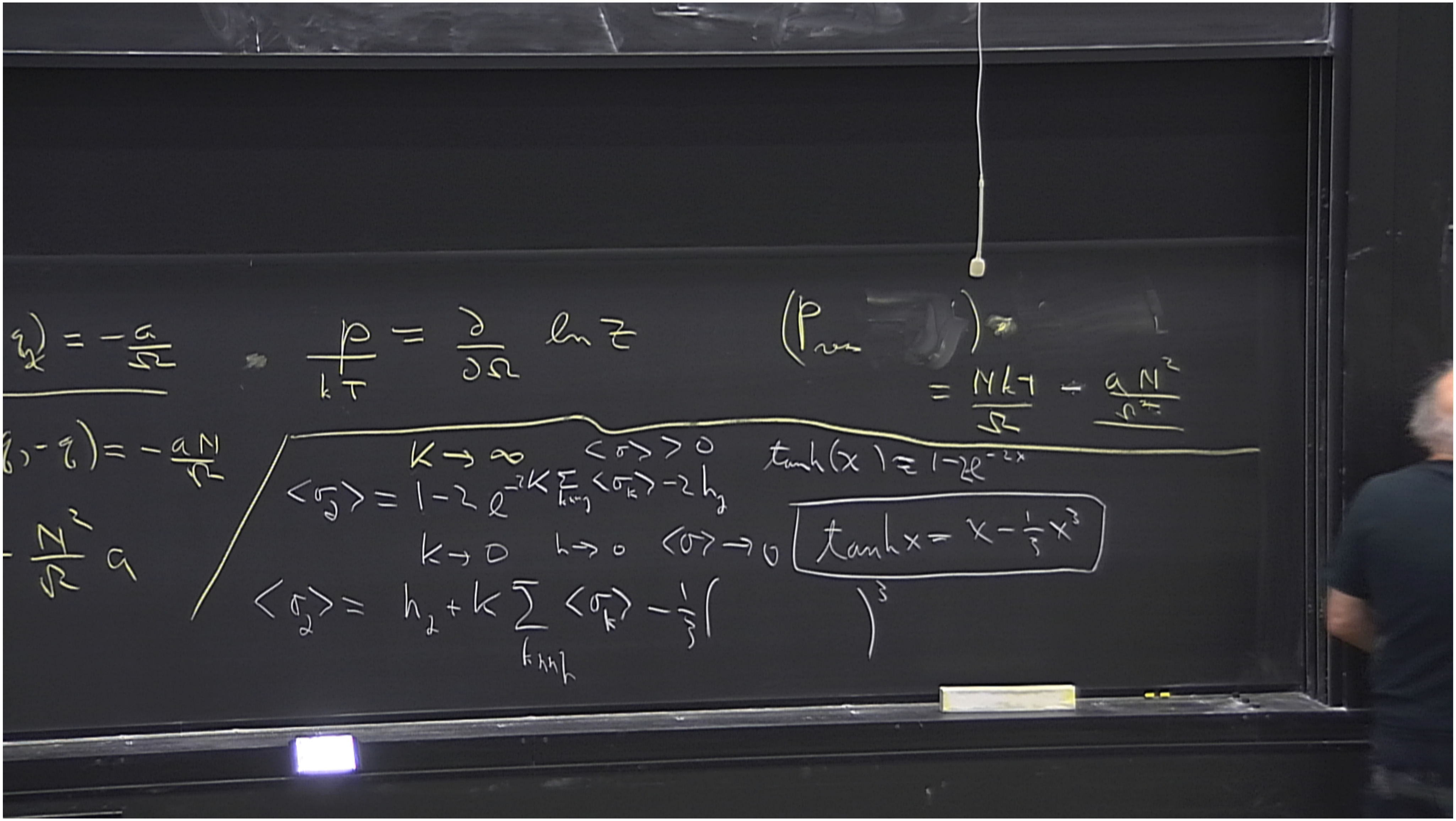

⟨σ⟩ = tanh h
H_eff = (h_j + K Σ_{k nn j} σ_k) σ_j
= tanh
H = hσ   σ±1
H = Σ_j h σ_j + Σ_{⟨jk⟩} σ_j σ_k K

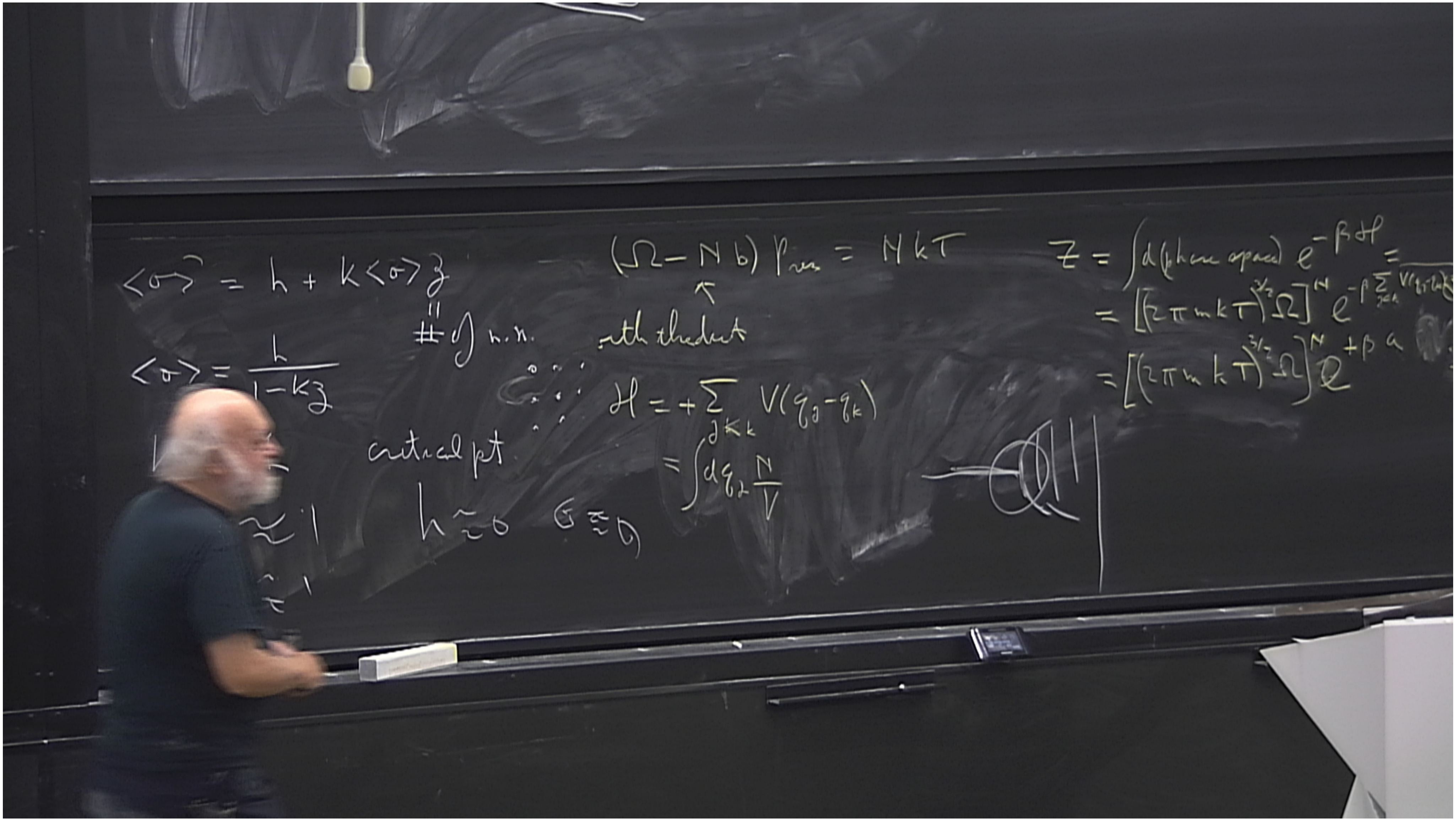

$\langle\sigma\rangle = \tanh h$
$\mathcal{H}_{eff} = \left(h_j + K \sum_{k\, nn\, j} \sigma_k\right)\sigma_j$
$\langle\sigma_j\rangle = \tanh\left(h_j + K \sum_{k\, nn\, j} \langle\sigma_k\rangle\right)$
$\mathcal{H} = h\sigma \quad \sigma \pm 1$
$\mathcal{H} = \sum_j h\sigma_j + \sum_{\langle jk\rangle} \sigma_j\sigma_k K$


$\langle \sigma \rangle = \tanh h$
$H = h\sigma \quad \sigma \pm 1$
$H_{eff} = (h_j + K \sum_{k\, nn\, j} \sigma_k)\sigma_j$
$H = \sum_j h \sigma_j + \sum_{\langle jk \rangle} \sigma_j \sigma_k K$
$\langle \sigma_j \rangle = \tanh(h_j + K \sum_{k\, nn\, j} \langle \sigma_k \rangle)$
m.f.t.


$V(q, -q) = -\frac{a}{\Omega}$
$\int dq \, V(q, -q) = -\frac{aN}{\Omega}$
$-\frac{aN}{\Omega} = -\frac{N^2}{\Omega} a$
$\frac{p}{kT} = \frac{\partial}{\partial \Omega} \ln Z$
$= \frac{NkT}{\Omega} - \frac{aN^2}{\Omega^2}$
$K \to \infty \quad \langle \sigma \rangle > 0 \quad \tanh(x) \approx 1 - 2e^{-2x}$
$\langle \sigma_j \rangle = 1 - 2 e^{-2K \sum_{k \in j} \langle \sigma_k \rangle - 2h_j}$
$K \to 0 \quad h \to 0 \quad \langle \sigma \rangle \to 0 \quad \tanh x = x - \frac{1}{3}x^3$
$\langle \sigma_j \rangle =$


p/kT = ∂/∂Ω ln Z
= NkT/Ω − aN²/Ω²
⟨σ⟩ > 0
tanh(x) ≈ 1−2e^{−2x}
k → 0   h → 0   ⟨σ⟩ → 0
tanh x = x − 1/3 x³


$\frac{p}{kT} = \frac{\partial}{\partial \Omega} \ln Z$
$= \frac{NkT}{\Omega} - \frac{aN^2}{\Omega^2}$
$K \to \infty \quad \langle \sigma \rangle > 0 \quad \tanh(x) \approx 1 - 2e^{-2x}$
$\langle \sigma_j \rangle = 1 - 2\, e^{-2K \sum_{k nn j} \langle \sigma_k \rangle - 2h_j}$
$k \to 0 \quad h \to 0 \quad \langle \sigma \rangle \to 0$
$\boxed{\tanh x = x - \frac{1}{3} x^3}$
$\langle \sigma_j \rangle = h_j + K \sum_{k nn j} \langle \sigma_k \rangle - \frac{1}{3} (\quad)^3$


critical pt
Z = ∫d(phase space) e^{-βH}