Title: Statistical Physics Lecture - 111523

Speakers: Emilie Huffman

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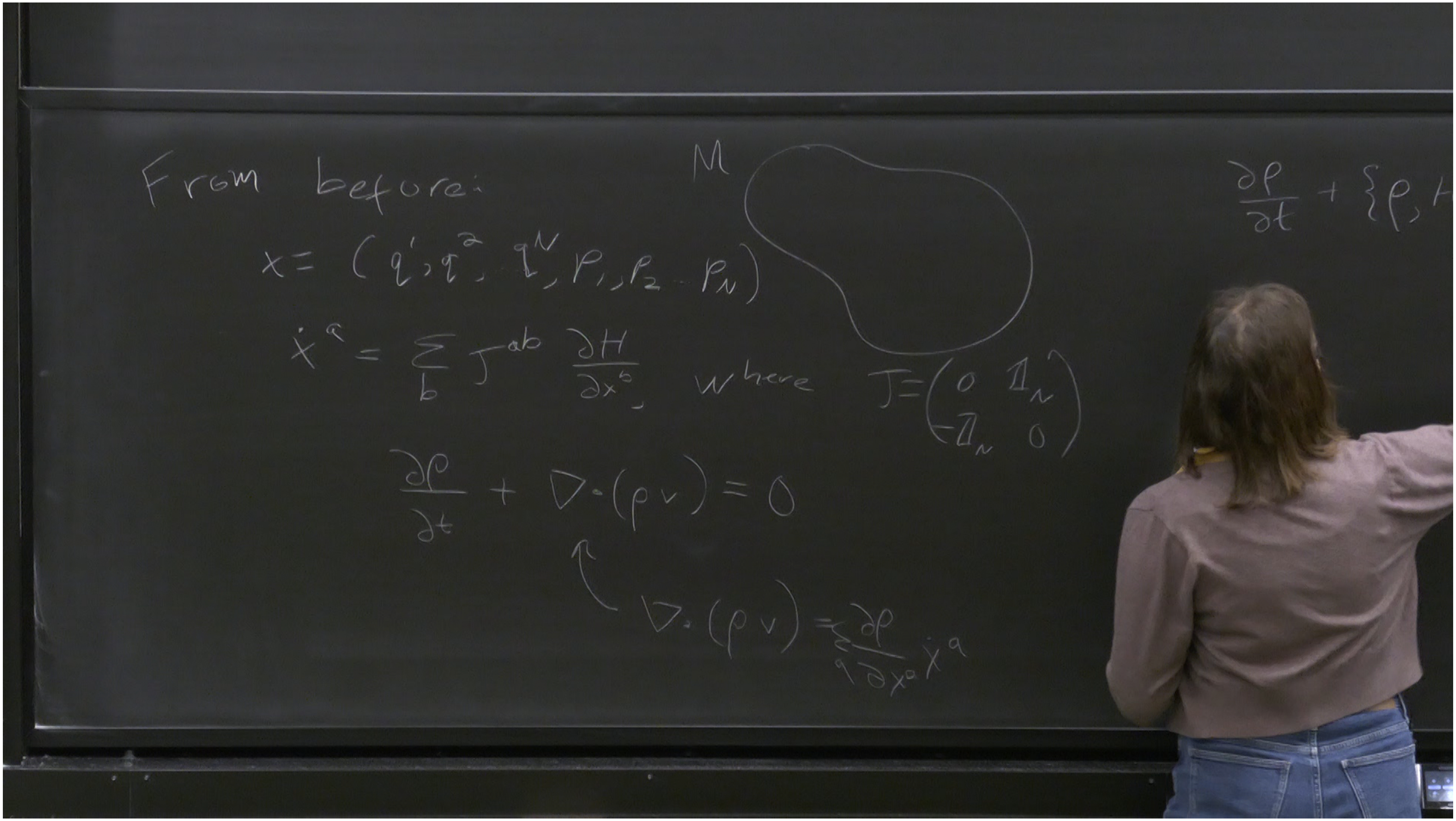
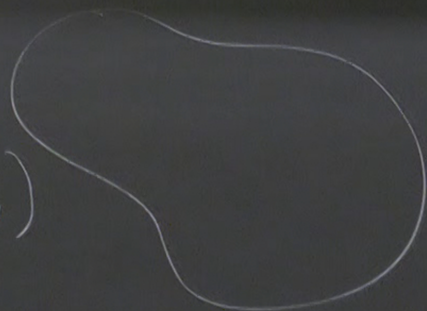

From before:
$x = (q^1, q^2, \ldots q^N, p_1, p_2 \ldots p_N)$
M
$\dot{x}^a = \sum_b J^{ab} \frac{\partial H}{\partial x^b}$, where $J = \begin{pmatrix} 0 & \mathbb{1}_N \\ -\mathbb{1}_N & 0 \end{pmatrix}$
$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = 0$
$\nabla \cdot (\rho v) = \sum_a \frac{\partial \rho}{\partial x^a} \dot{x}^a$
$\frac{\partial \rho}{\partial t} + \{\rho, H$

M



$, p_2 \ldots p_N)$

where $J = \begin{pmatrix} 0 & \mathbb{1}_N \\ -\mathbb{1}_N & 0 \end{pmatrix}$

$(\rho v) = 0$

$\nabla \cdot (\rho v) = \sum_a \frac{\partial \rho}{\partial x^a} \dot{x}^a$

$$\boxed{\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0}$$ ← Liouville's equation

$$\frac{d}{dt} \rho(x(t), t) = \left(\frac{\partial \rho}{\partial t} + \{\rho, H\} \right) \Bigg|_{x(t), t} = 0$$

ρ is constant along trajectories in phase space.

Equilibrium: $\frac{\partial \rho}{\partial t}$

$$\boxed{\{\rho, H\} = 0}$$

E

B

Z

C

$\nabla \cdot (\rho v) = \sum_a \frac{\partial \rho}{\partial x^a} \dot{x}^a$

$\{\rho, H\} = ($

Gibbs Entropy

Allows us to define the entropy (S) of a macrostate the weights (ρ) of the microstates.

We know that for a state λ,

$$P_\lambda = \frac{\rho_\lambda}{\sum_\lambda \rho_\lambda}$$

is the prob. of a system being in state λ.

from

The Gibbs entropy is then

$$S = -k \sum_{\lambda} P_{\lambda} \ln(P_{\lambda})$$

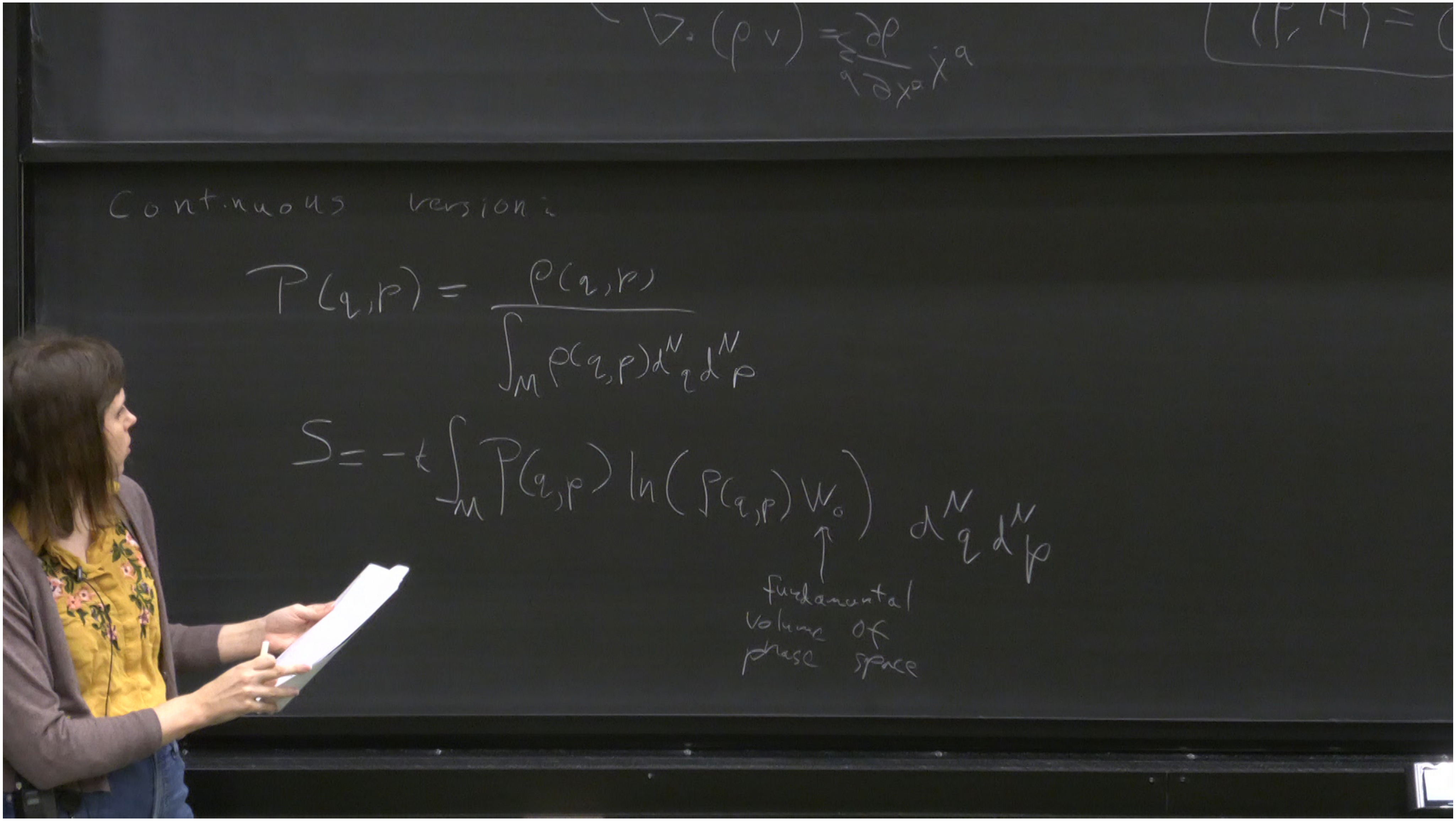
↑ Boltzmann

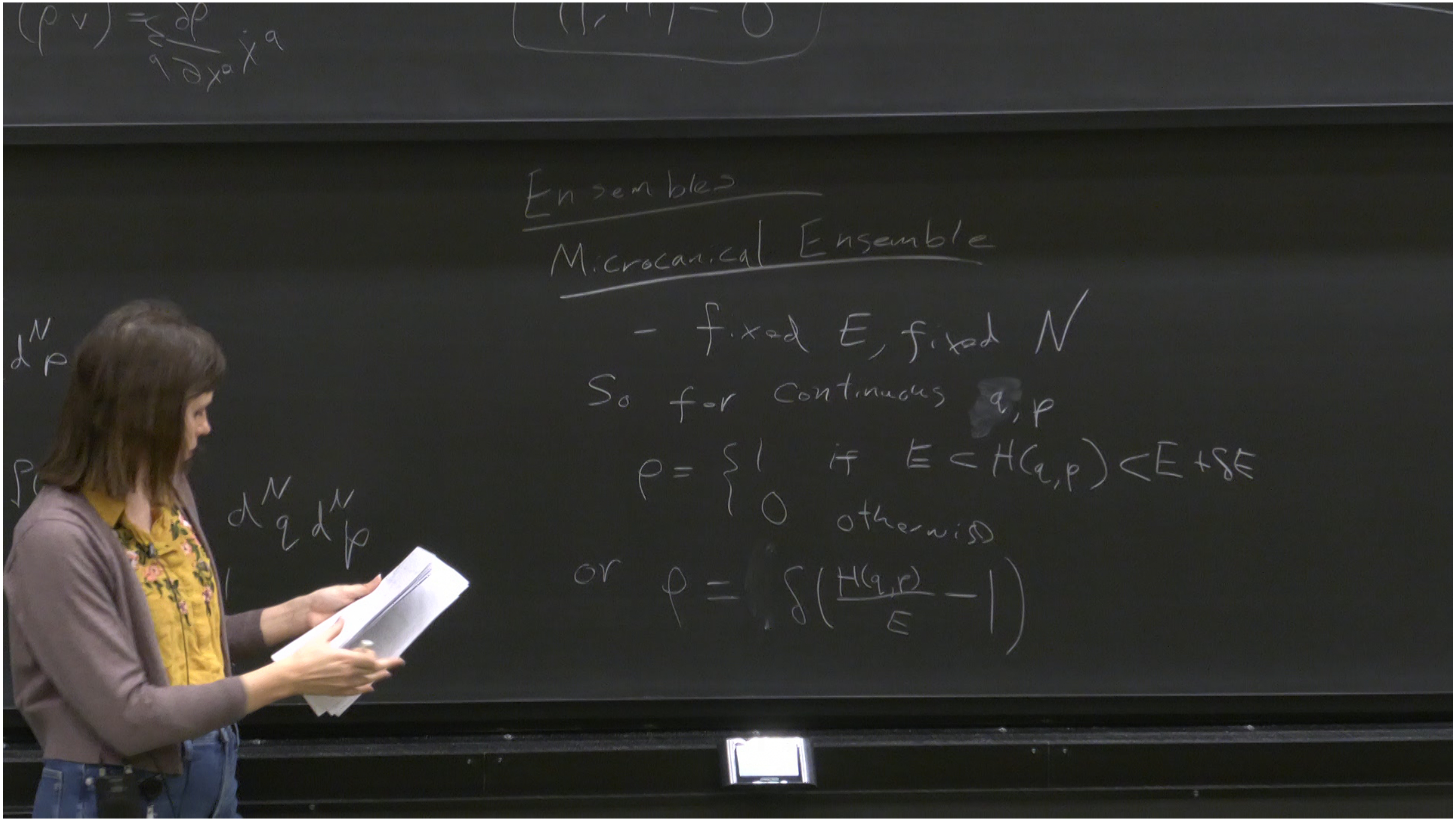
Suppose that

$$P_{\lambda} = \begin{cases} 1 & \text{for accessible configurations } \swarrow W \\ 0 & \text{otherwise} \end{cases}$$

$$S = -k \sum_{\lambda} \frac{1}{W} \ln\left(\frac{1}{W}\right) = -k \frac{1}{W} \ln\left(\frac{1}{W}\right) \underbrace{\left(\sum_{\lambda} 1\right)}_{W}$$

$$= -k \ln\left(\frac{1}{W}\right) = k \ln(W) \geq 0$$


$\nabla \cdot (\rho v) = \sum_a \frac{\partial \rho}{\partial x^a} \dot{x}^a$
Continuous version:
$P(q,p) = \frac{\rho(q,p)}{\int_M \rho(q,p) d^N q \, d^N p}$
$S = -k \int_M P(q,p) \ln(\rho(q,p) W_0) \, d^N q \, d^N p$
fundamental volume of phase space


Ensembles
Microcanonical Ensemble
- fixed E, fixed N
So for continuous q, p
$\rho = \begin{cases} 1 & \text{if } E < H(q,p) < E + \delta E \\ 0 & \text{otherwise} \end{cases}$
or $\rho = \delta\left(\frac{H(q,p)}{E} - 1\right)$

ple

ited N

s q, p

$E < H(q,p) < E + \delta E$

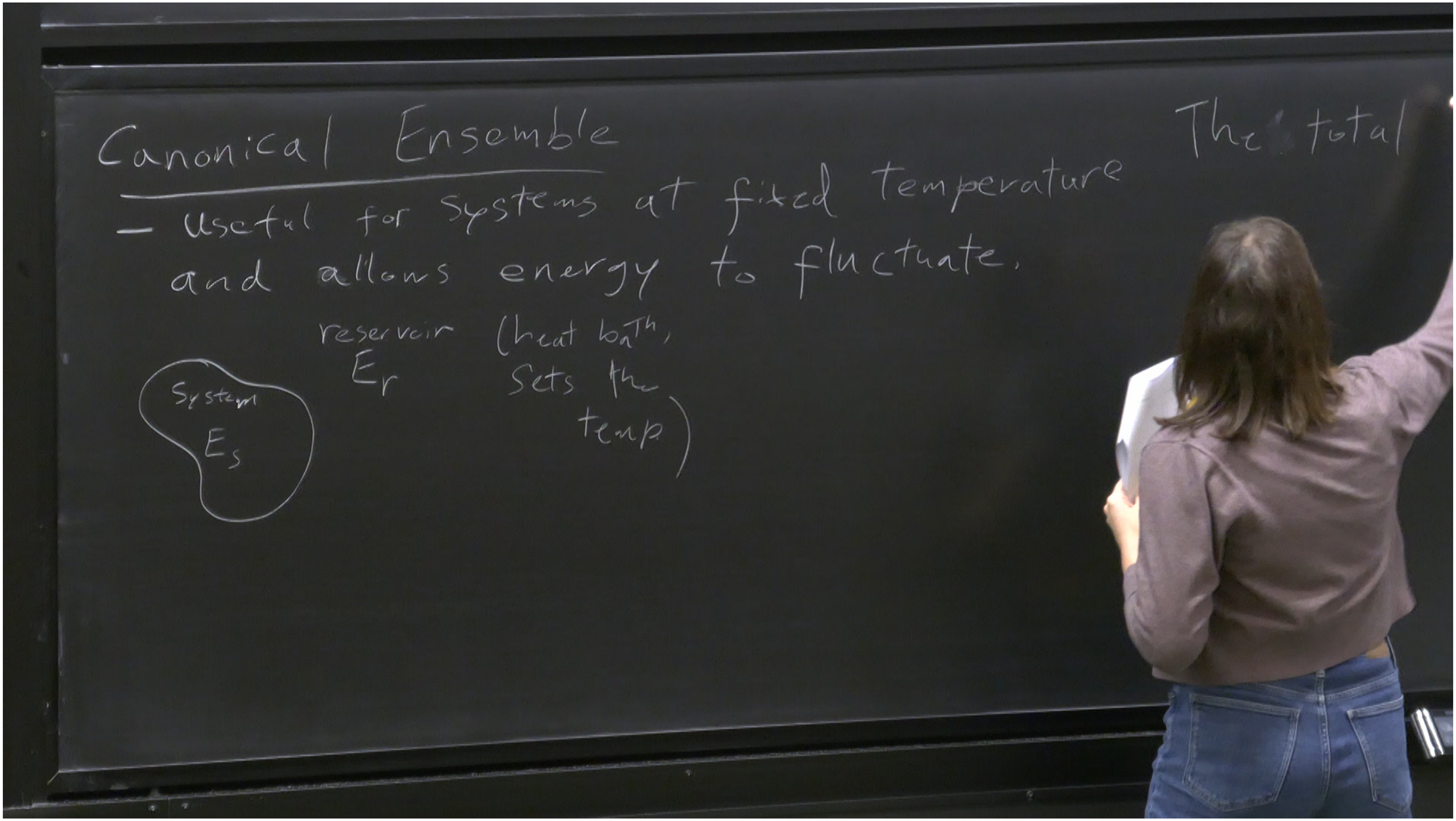
wise)

$-1)\big)$

So then

$$W = \int_M \rho \, d^N q \, d^N p$$

$$S = k \ln\left(W/W_0\right)$$


Canonical Ensemble
- Useful for systems at fixed temperature and allows energy to fluctuate.
reservoir (heat bath, sets the temp)
E_r
System
E_s
The total

e

s at fixed temperature

rgy to fluctuate.

bath,

the

temp)

The total Energy is:

$$E_s + E_r = E^{(0)} = \text{const.}$$

$$E_s \ll E^{(0)}$$

$$\rho(p_s, q_s) \propto W(E_r)$$

system

$$\ln(\rho(p,q)) \propto \ln(W(E_r))$$

expand about $E_r = E^{(0)}$

$$\ln(\rho(p,q)) \propto \ln(E^{(0)}) + \frac{\partial \ln W(E)}{\partial E}\Big|_{E=E^{(0)}} (E_r - E^{(0)})$$

...le

...s at fixed temperature

...rgy to fluctuate.

bath,

the

temp)

The total Energy is:

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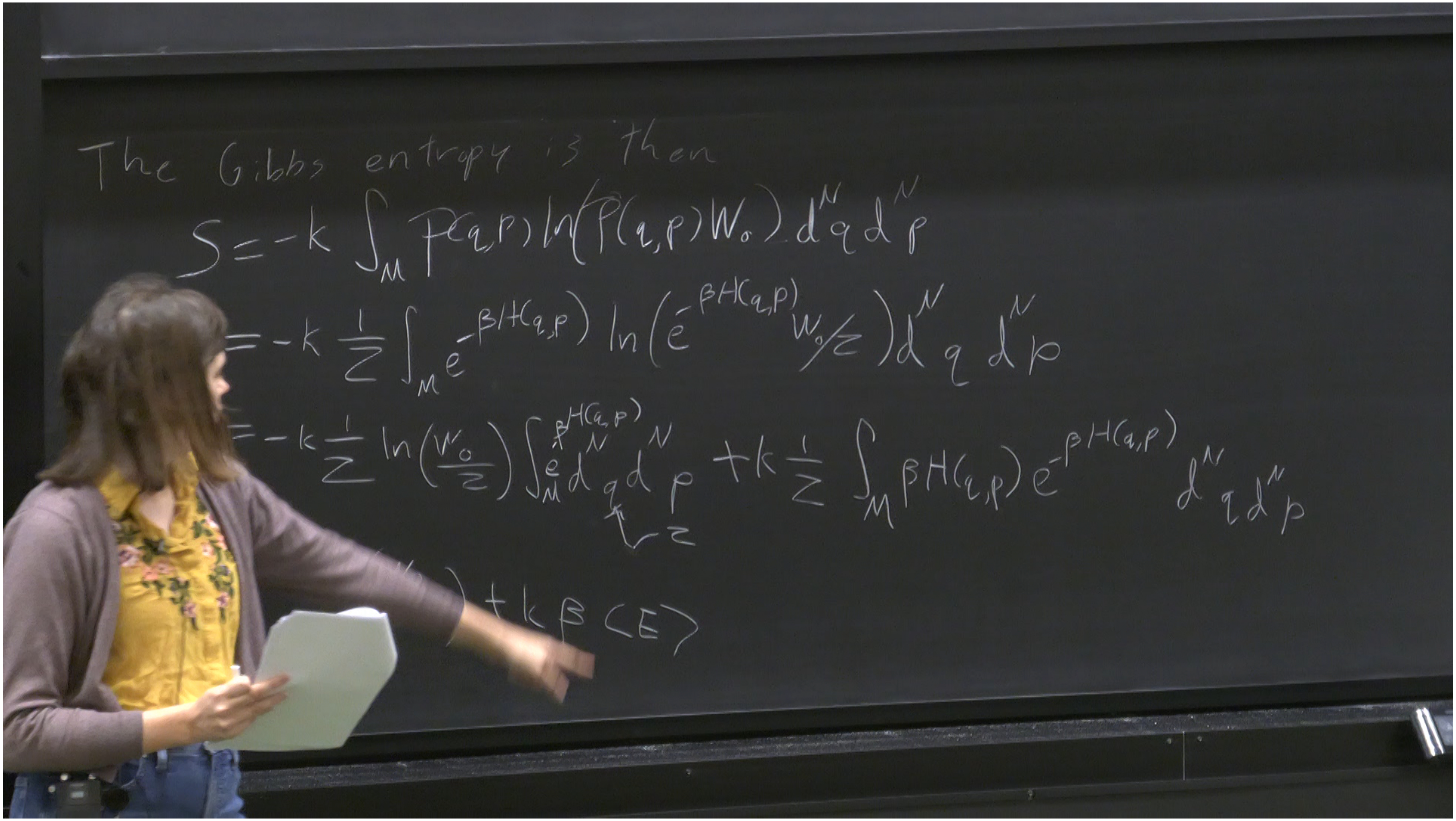
$$\ln(\rho(p,q)) \propto \ln(E^{(0)}) + \frac{\partial \ln W(E)}{\partial E}\bigg|_{E=E^{(0)}} (E_r - E^{(0)})$$

$$= \text{const.} - \beta E_S \qquad \frac{\partial S}{\partial E} = \frac{1}{kT} \qquad P(q,p) = \frac{e^{-\beta H(q,p)}}{Z}$$

$$\rho(q,p) \propto e^{-\beta H(q,p)}$$

For continuous system, we can define a partition function

$$Z = \int_M e^{-\beta H(q,p)} d^N q \, d^N p$$


The Gibbs entropy is then
$S = -k \int_M \rho(q,p) \ln(\rho(q,p) W_0)\, d^N q\, d^N p$
$= -k \frac{1}{Z} \int_M e^{-\beta H(q,p)} \ln\left(e^{-\beta H(q,p)} W_0/Z\right) d^N q\, d^N p$
$= -k \frac{1}{Z} \ln\left(\frac{W_0}{Z}\right) \int_M e^{-\beta H(q,p)} d^N q\, d^N p + k \frac{1}{Z} \int_M \beta H(q,p) e^{-\beta H(q,p)} d^N q\, d^N p$
$= Z$
$+ k\beta \langle E \rangle$

...en

$$\ldots,p)W_0)\, d^N q\, d^N p$$

$$\left(e^{-\beta H(q,p)} W_0/Z\right) d^N q\, d^N p$$

$$\ldots p + k\frac{1}{Z}\int_M \beta H(q,p)\, e^{-\beta H(q,p)}\, d^N q\, d^N p$$

$\ldots Z$

$\ldots >$

To get to thermodynamics:

$$F = U - TS = -kT\ln\left(\frac{Z}{W_0}\right)$$

What is the free energy?

$$Z = \sum_{(p,q)} e^{-\beta H(p,q)}$$

$$= \sum_E \omega(E)\, e^{-\beta E}$$

states with this energy

$$= \sum_E e^{-\beta E + \ln \omega(E)}$$

$$= \sum_E e^{-\beta E + \frac{1}{k} S(E)} \sim e^{-\beta (U - TS)} = e^{-\beta F}$$

At equilibrium:

At zero temperature, we mini

energy?

$e^{-\beta E}$

energy

(E)

At equilibrium:

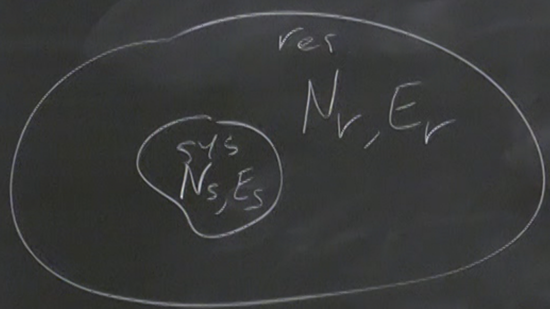
At zero temperature, we minimize energy

At finite temperature, we minimize free energy.

$(E) \sim e^{-\beta(U-TS)} = e^{-\beta F}$

Grand Canonical Ensemble

Now we allow both N and E to fluctuate.



$$E_s + E_r = E^{(0)}$$

$$N_s + N_r = N^{(0)}$$

$$P_s \propto W(E_r, N_r)$$

$$\ln P_s \simeq \ln W(N^{(0)}, E^{(0)}) + \left(\frac{\partial \ln W}{\partial N}\right)_{N=N^{(0)}} (N_r - N^{(0)} \ldots$$

$\ldots E_r - E^{(0)}$

$\ln$

$$\ln P_s \simeq \text{const.} - \frac{1}{kT} E_s + \frac{\mu}{kT} N_s$$

$$S = -k \sum_{N,\lambda} P_{N,\lambda} \ln\left(P_{N,\lambda}\right)$$

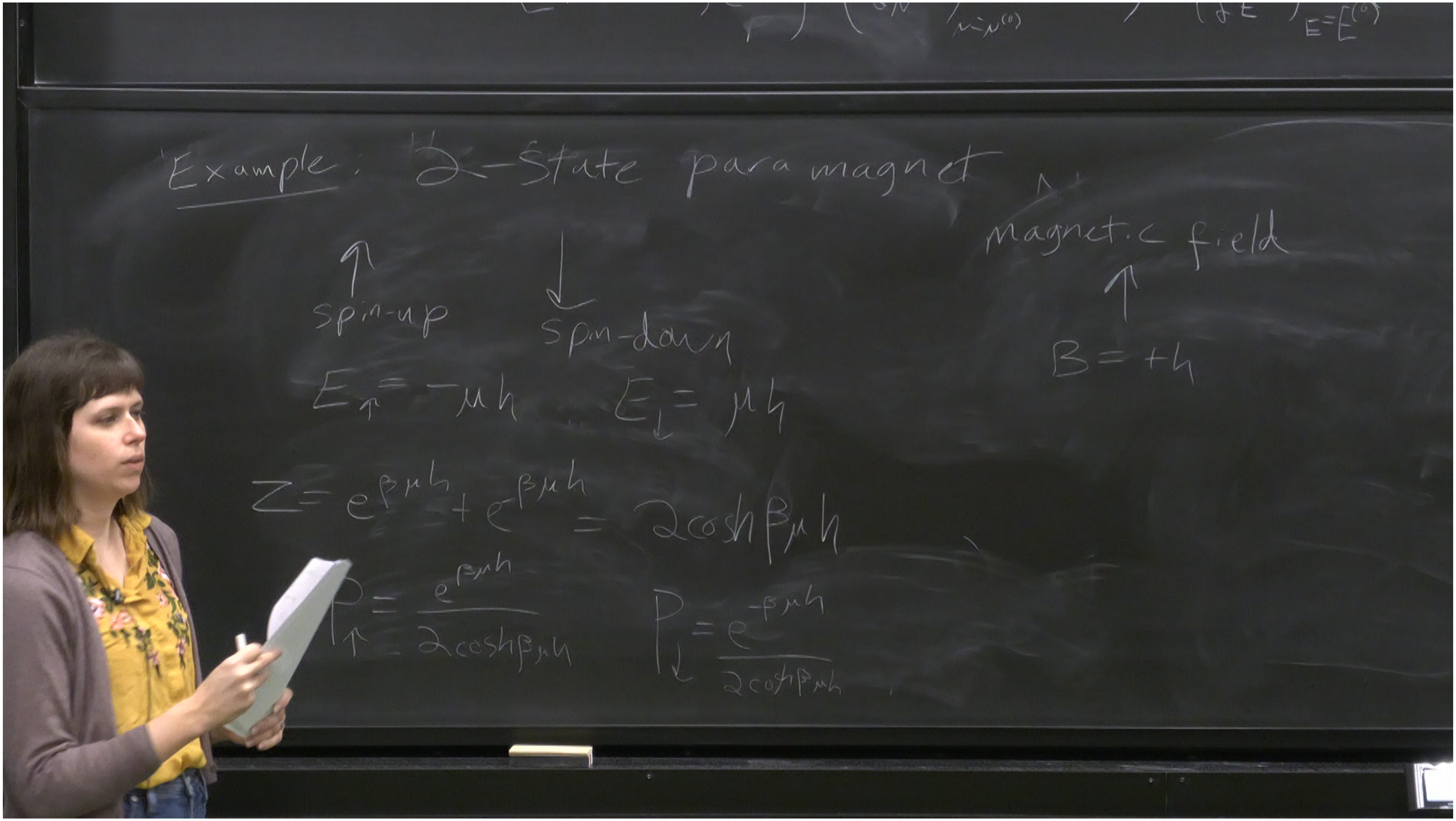
ato.

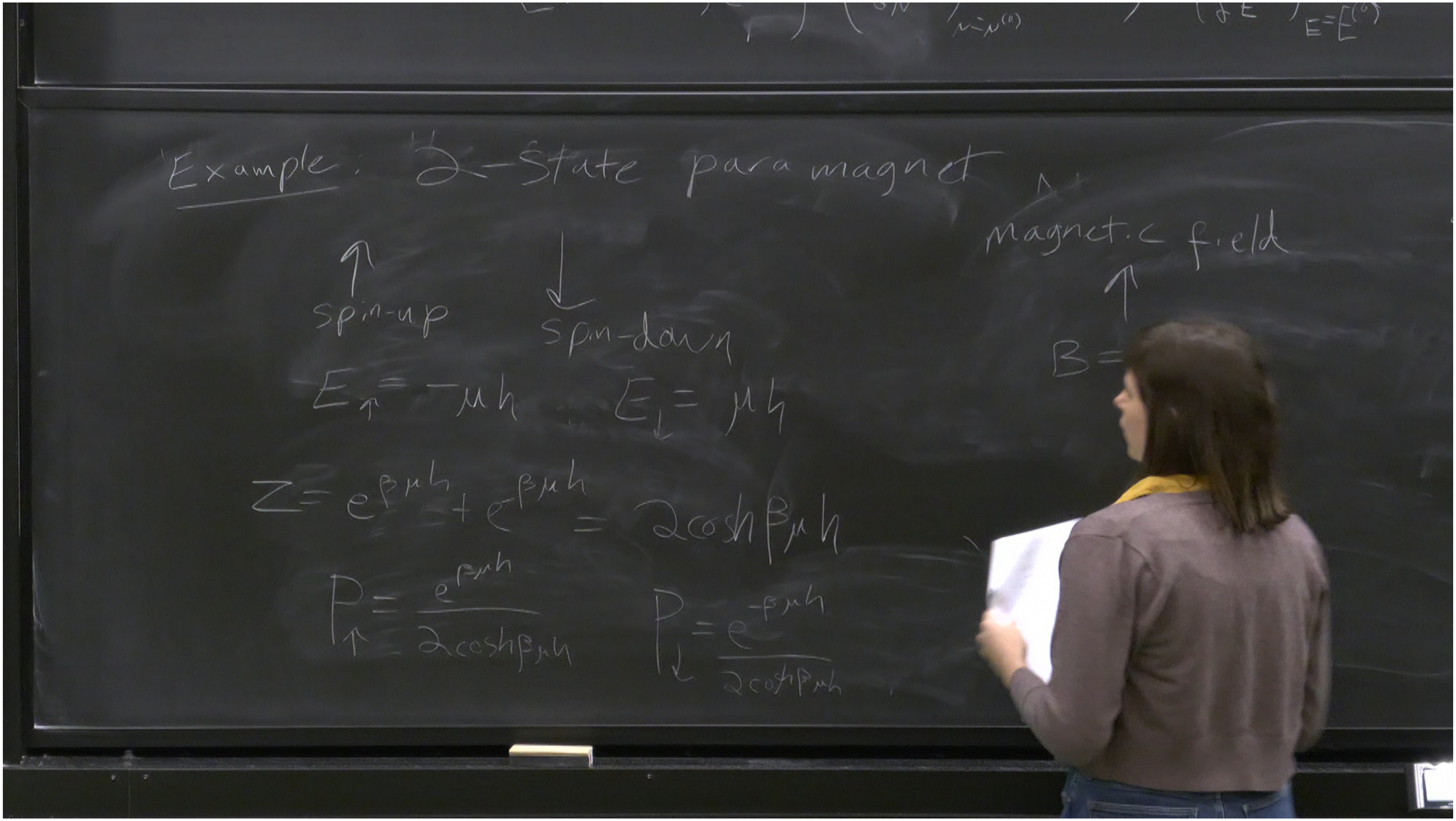
$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N$$

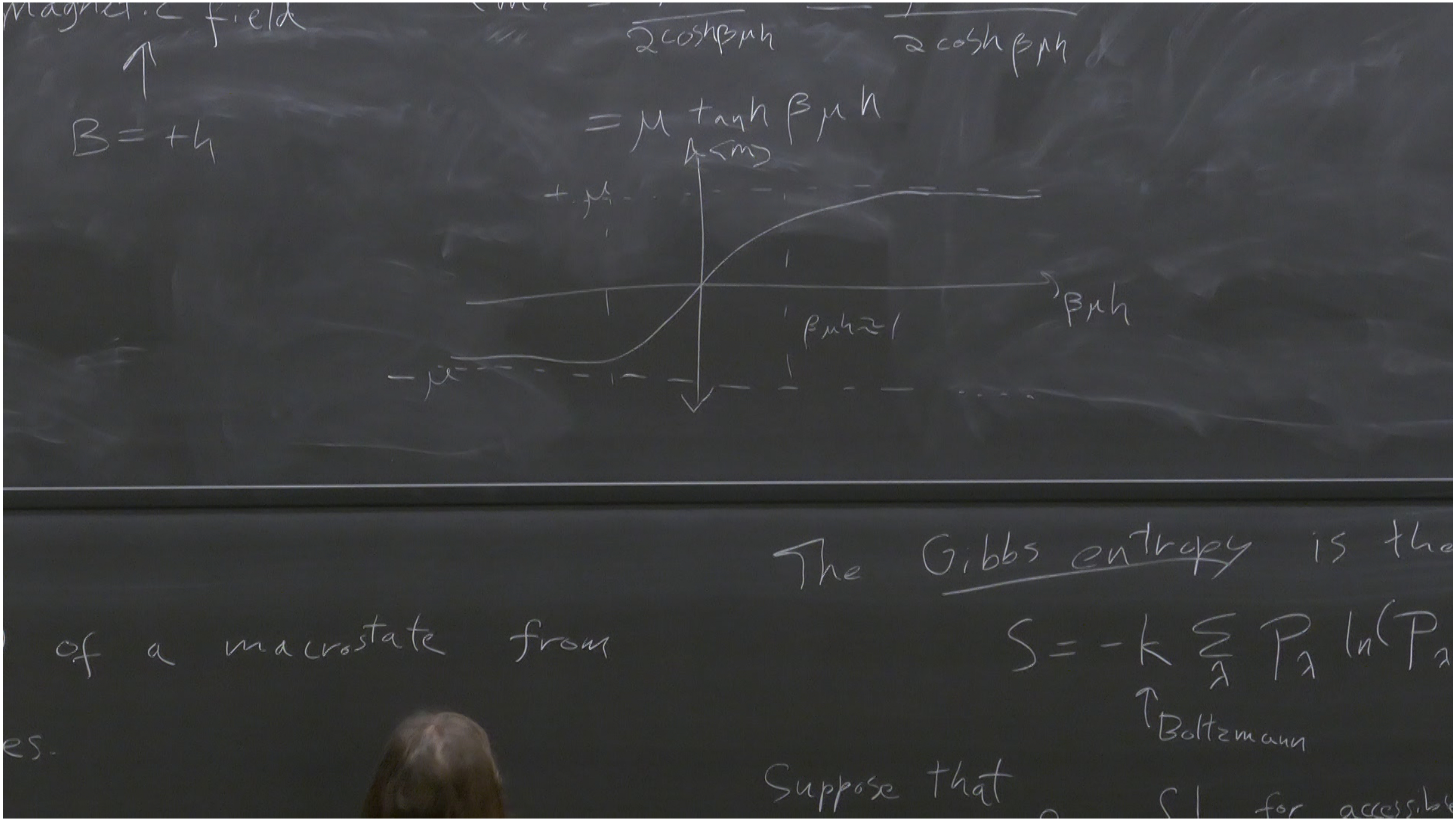
$$\Phi = PV = U - TS - \mu N$$

$$P_{N,\lambda} = \frac{e^{\beta\mu N - \beta E(\lambda, N)}}{\mathcal{Z}}$$

$$\ldots N^{(0)}\big) + \left(\frac{\partial \ln \Omega}{\partial E}\right)_{E=E^{(0)}} \left(E_r - E^{(0)}\right)$$


Example: 2-State paramagnet
magnetic field
spin-up
spin-down
B = +h
E↑ = −μh
E↓ = μh
Z = e^{βμh} + e^{−βμh} = 2cosh βμh
P↑ = e^{βμh} / 2cosh βμh
P↓ = e^{−βμh} / 2cosh βμh


Example: 2-State paramagnet
magnetic field
spin-up
spin-down
B =
$E_\uparrow = -\mu h$
$E_\downarrow = \mu h$
$Z = e^{\beta\mu h} + e^{-\beta\mu h} = 2\cosh\beta\mu h$
$P_\uparrow = \frac{e^{\beta\mu h}}{2\cosh\beta\mu h}$
$P_\downarrow = \frac{e^{-\beta\mu h}}{2\cosh\beta\mu h}$


field
2 cosh βμh
2 cosh βμh
B = +h
= μ tanh βμh
⟨m⟩
+μ
βμh
βμh ≃ 1
−μ
The Gibbs entropy is the
of a macrostate from
S = −k Σ_λ P_λ ln(P_λ
Boltzmann
es.
Suppose that
for accessible

$$P_\uparrow = \frac{\cdots}{2\cosh\beta\mu h} \qquad P_\downarrow = \frac{e^{\cdots}}{2\cosh\beta\mu h}$$

What if we had N paramagnets?

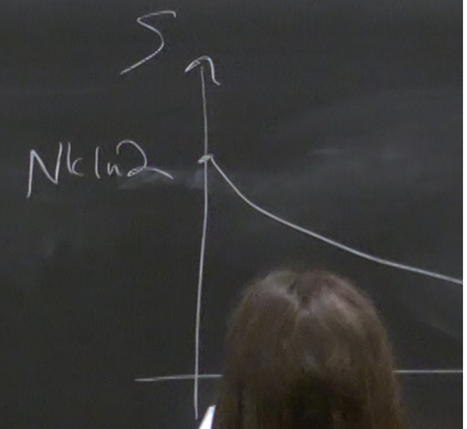
$$Z_1 = 2\cosh\beta\mu h$$

$$Z_N = Z_1^{\,N}$$

$$F = -kT\ln Z_N = -kTN\ln(2\cosh\beta\mu h)$$

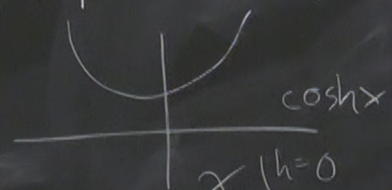
$$M = -\left(\frac{\partial F}{\partial h}\right)_T = N\mu\tanh\beta\mu h$$

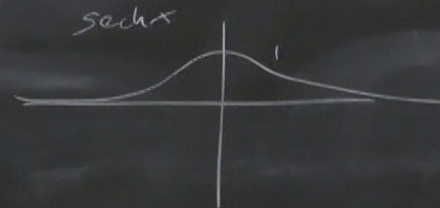
$$S = -\left(\frac{\partial F}{\partial T}\right)_h = Nk\ln(2\cosh\beta\mu h) - Nk\beta\mu h\tanh(\beta\mu h)$$

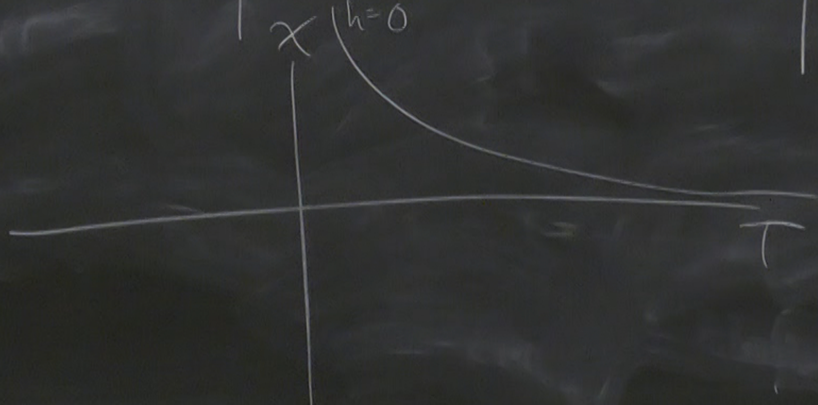


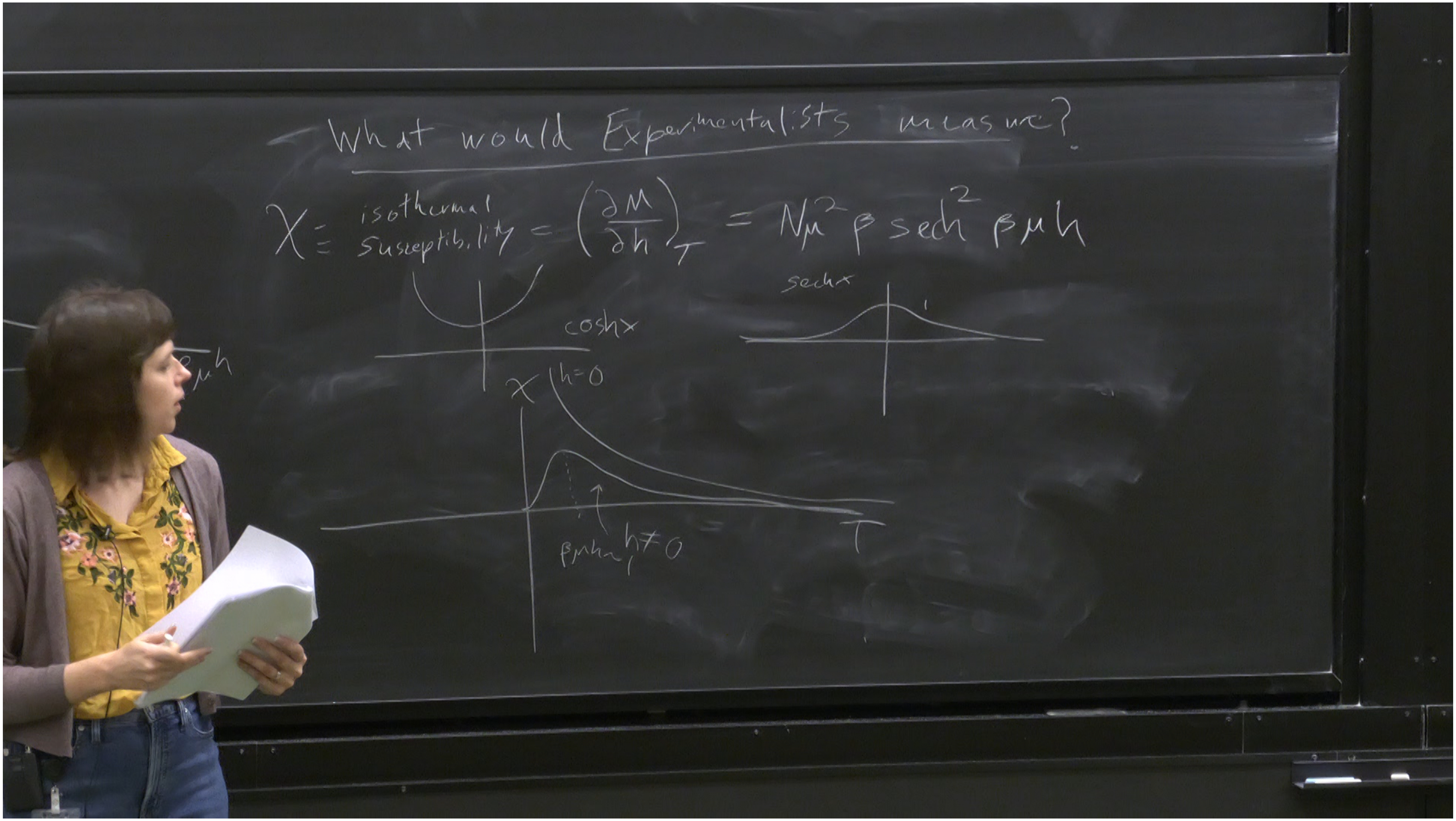
What would Experimentalists measure?

$$\chi \equiv \text{isothermal susceptibility} = \left(\frac{\partial M}{\partial h}\right)_T = N\mu^2 \beta \,\mathrm{sech}^2 \beta\mu h$$








What would Experimentalists measure?
$\chi \equiv$ isothermal susceptibility $= \left(\frac{\partial M}{\partial h}\right)_T = N\mu^2 \beta \operatorname{sech}^2 \beta\mu h$
cosh x
sech x
χ
h=0
h≠0
T