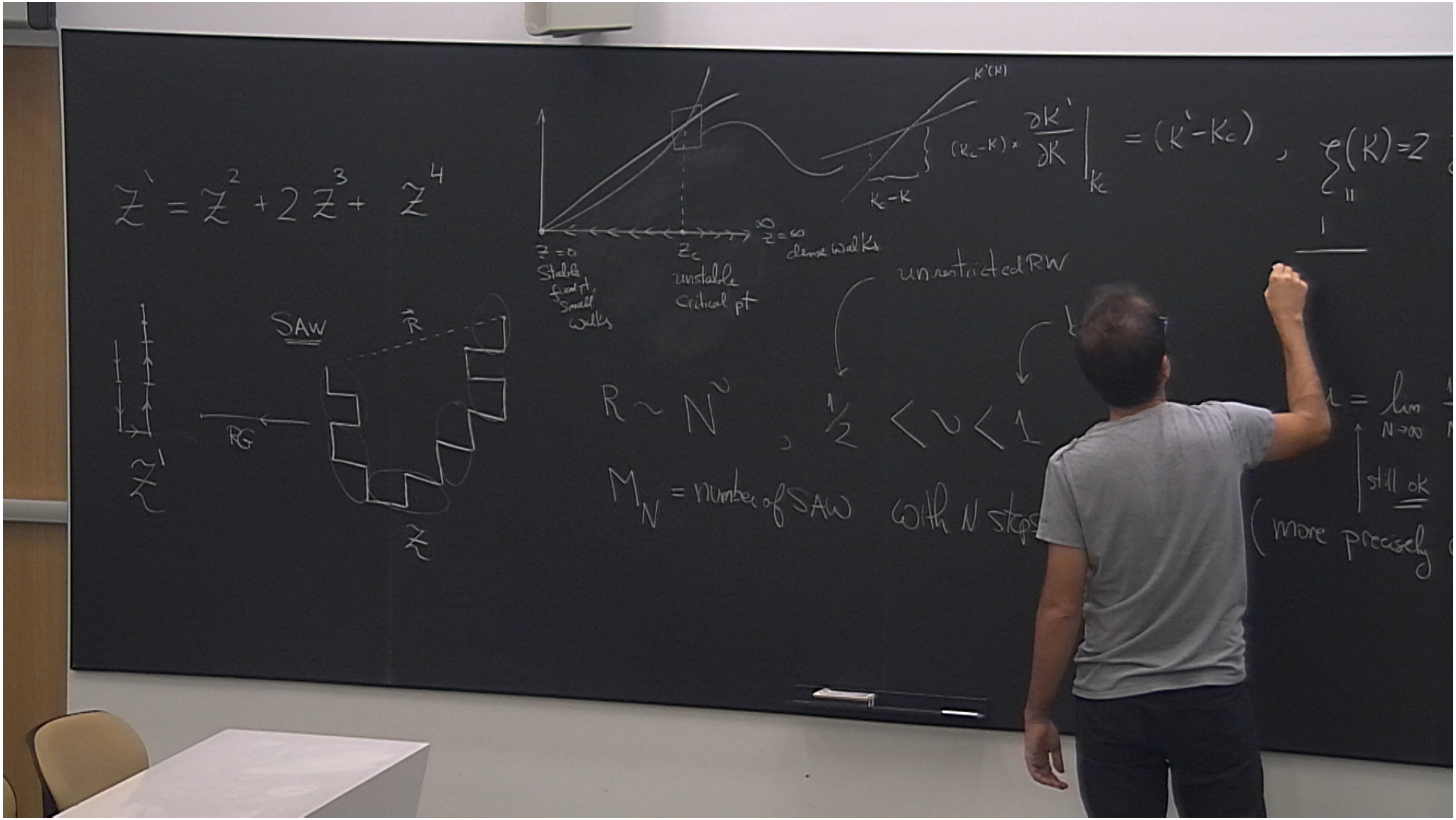
Title: PSI 2019/2020 - Statistical Mechanics (Vieira) - Lecture 13

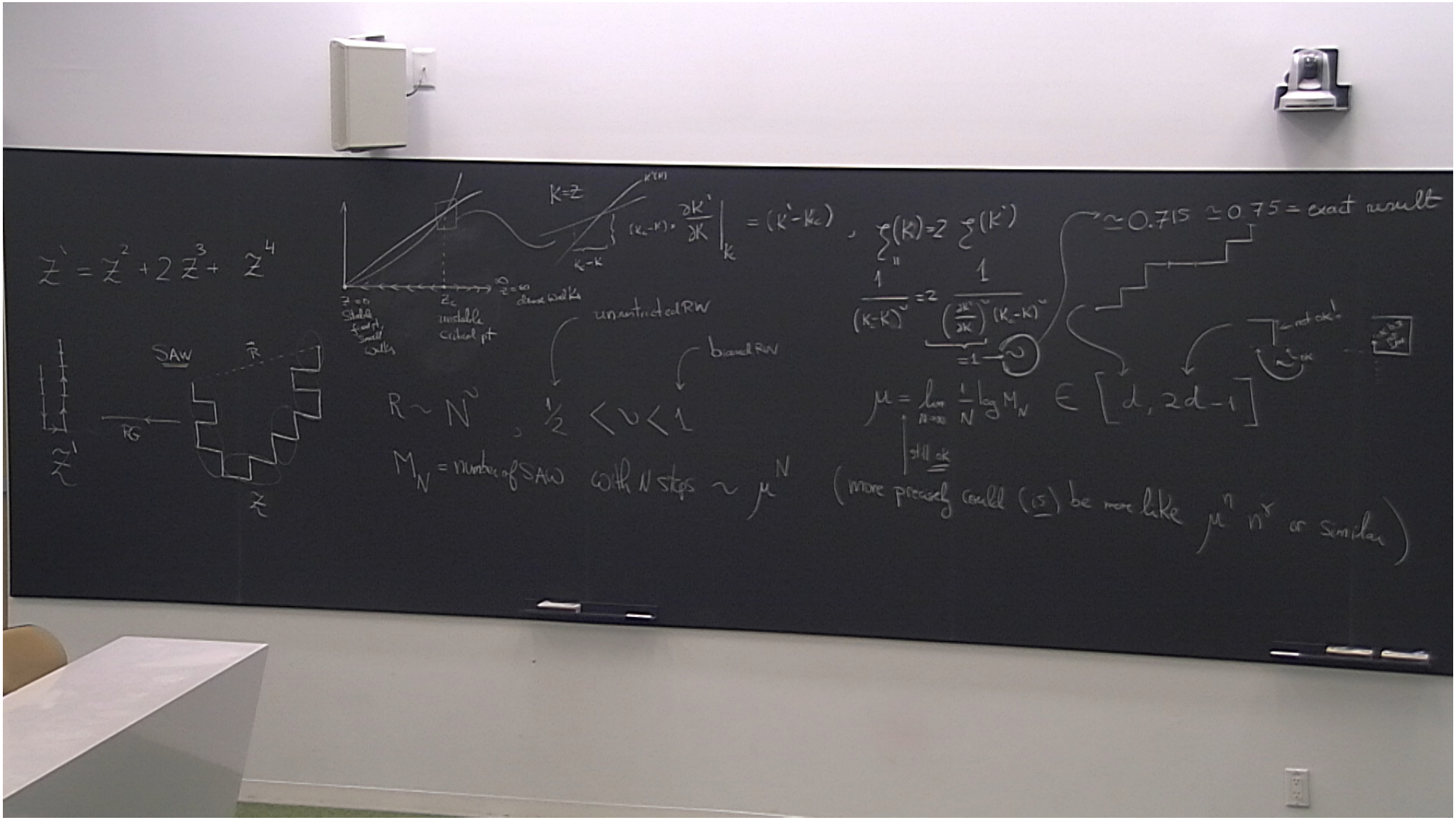
Speakers: Pedro Vieira

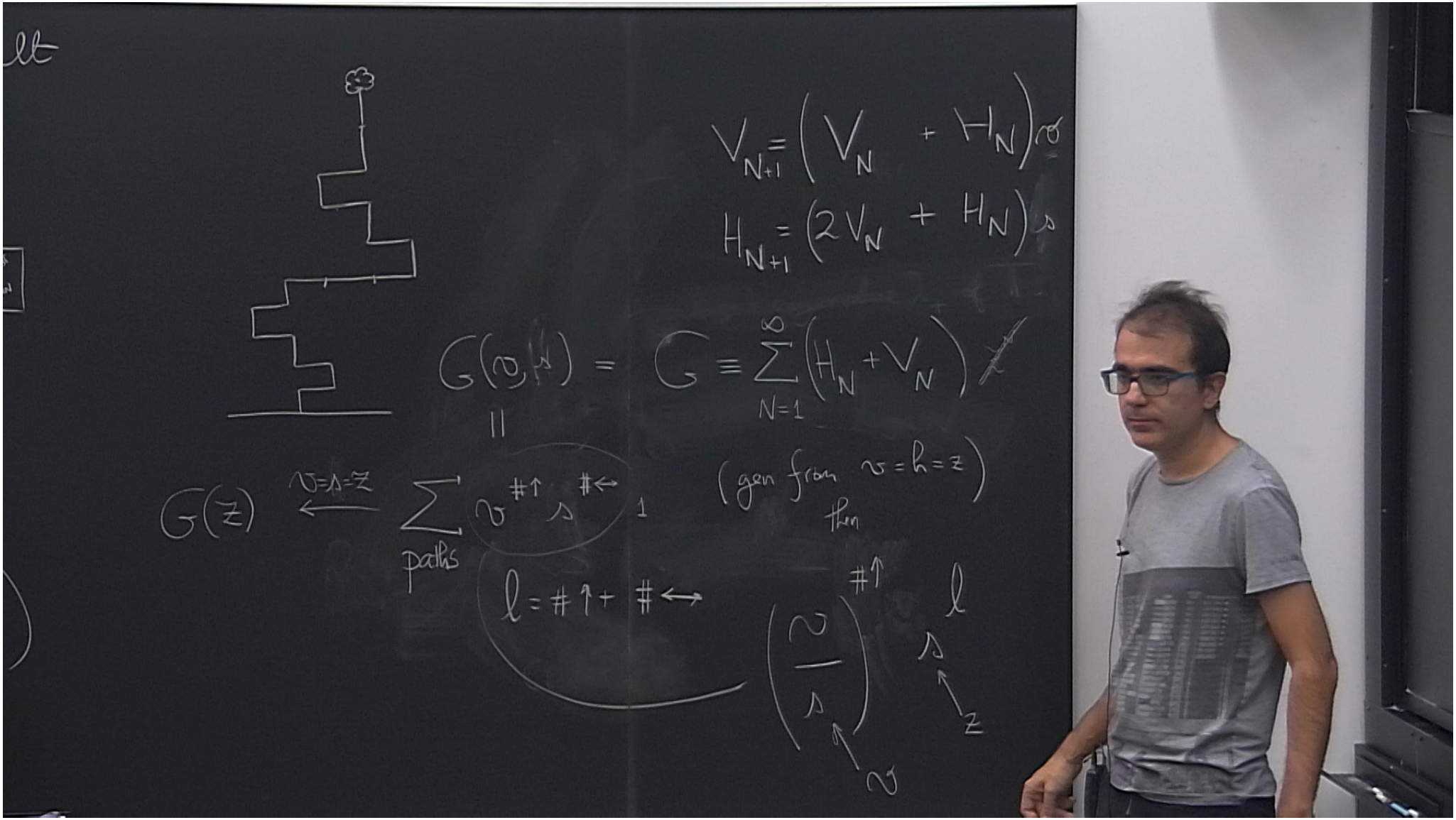
Collection: PSI 2019/2020 - Statistical Mechanics (Vieira)

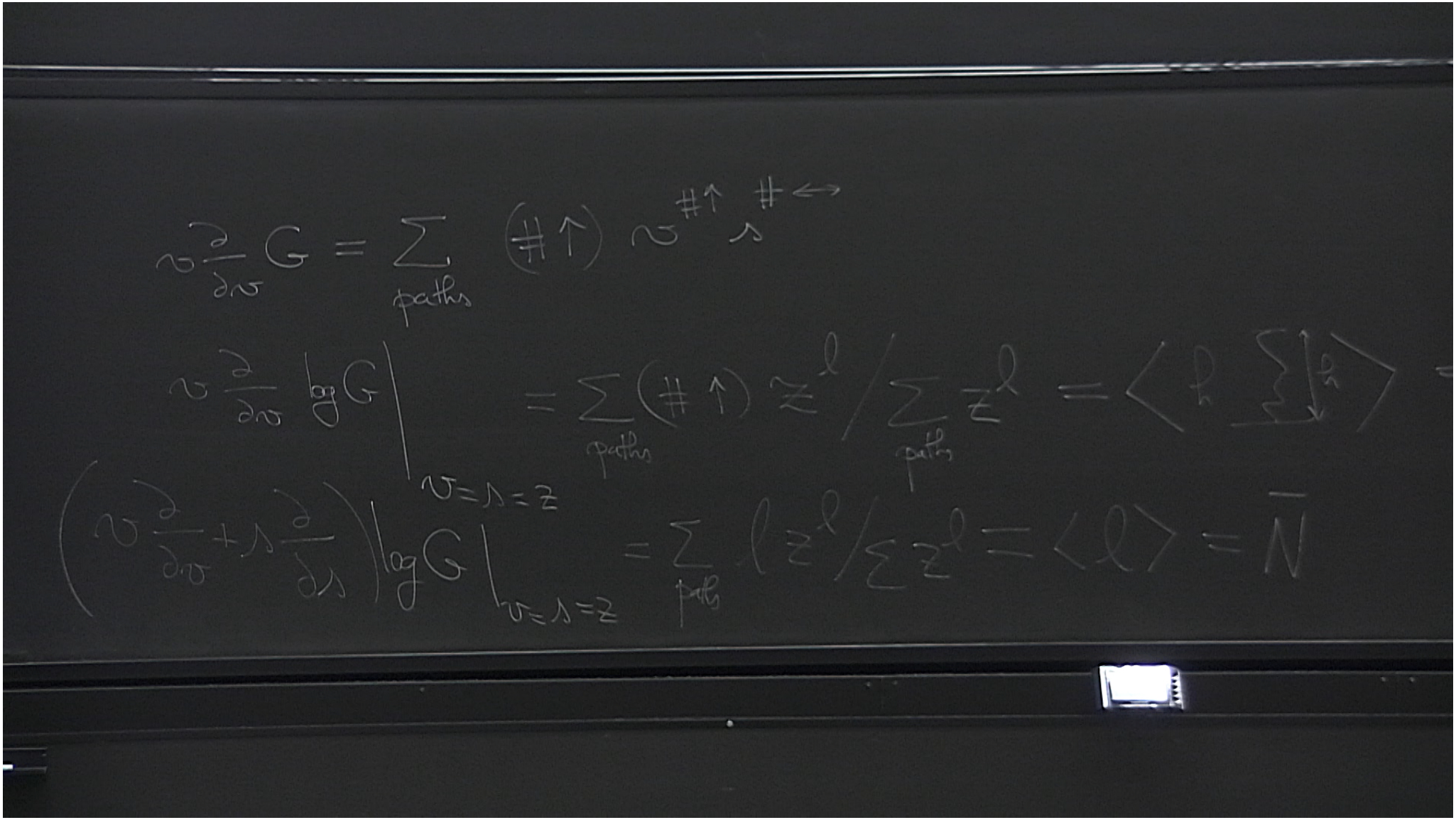
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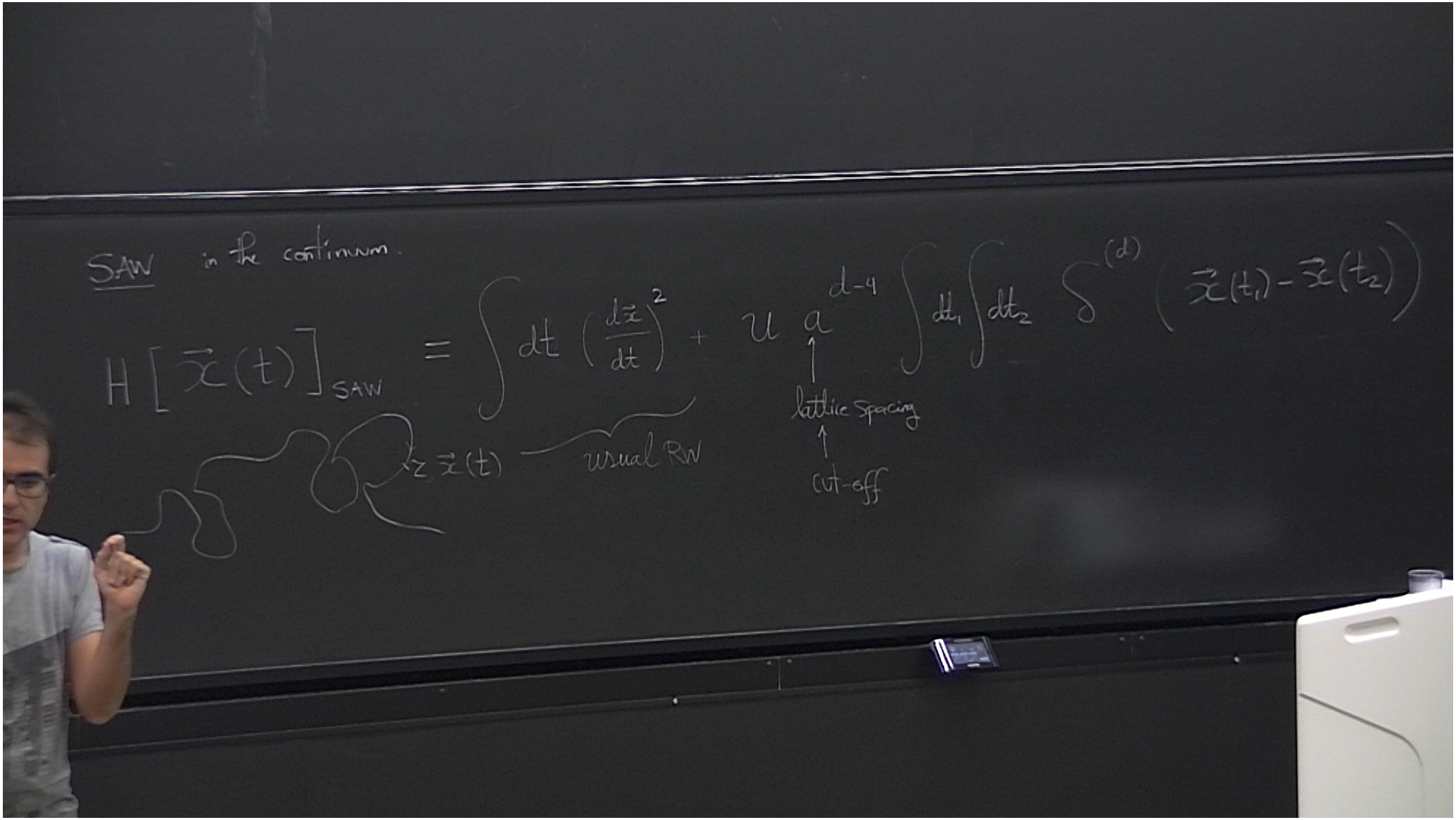
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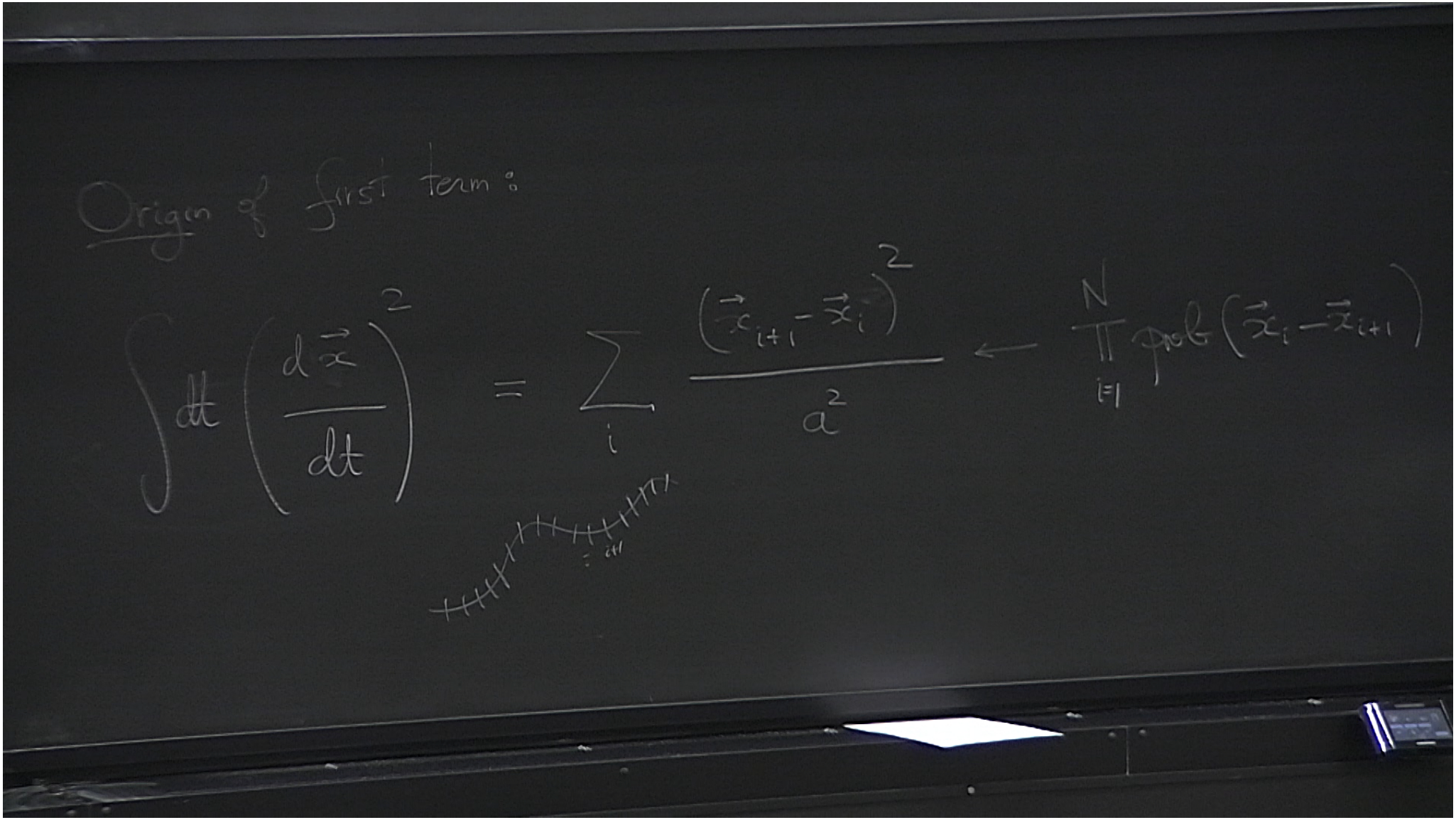

$z' = z^2 + 2z^3 + z^4$
K'(K)
$(K_c - K) \cdot \frac{\partial K'}{\partial K}\Big|_{K_c} = (K' - K_c)$
$\xi(K) = Z$
$K_c - K$
$z = 0$
Stable fixed pt, Small walks
z_c
unstable critical pt
$z = \infty$
dense walks
unrestricted RW
SAW
$\vec{R}$
RG
z'
z
$R \sim N^{\nu}$, $\frac{1}{2} < \nu < 1$
M_N = number of SAW with N steps
$\nu = \lim_{N \to \infty}$
still ok
(more precisely

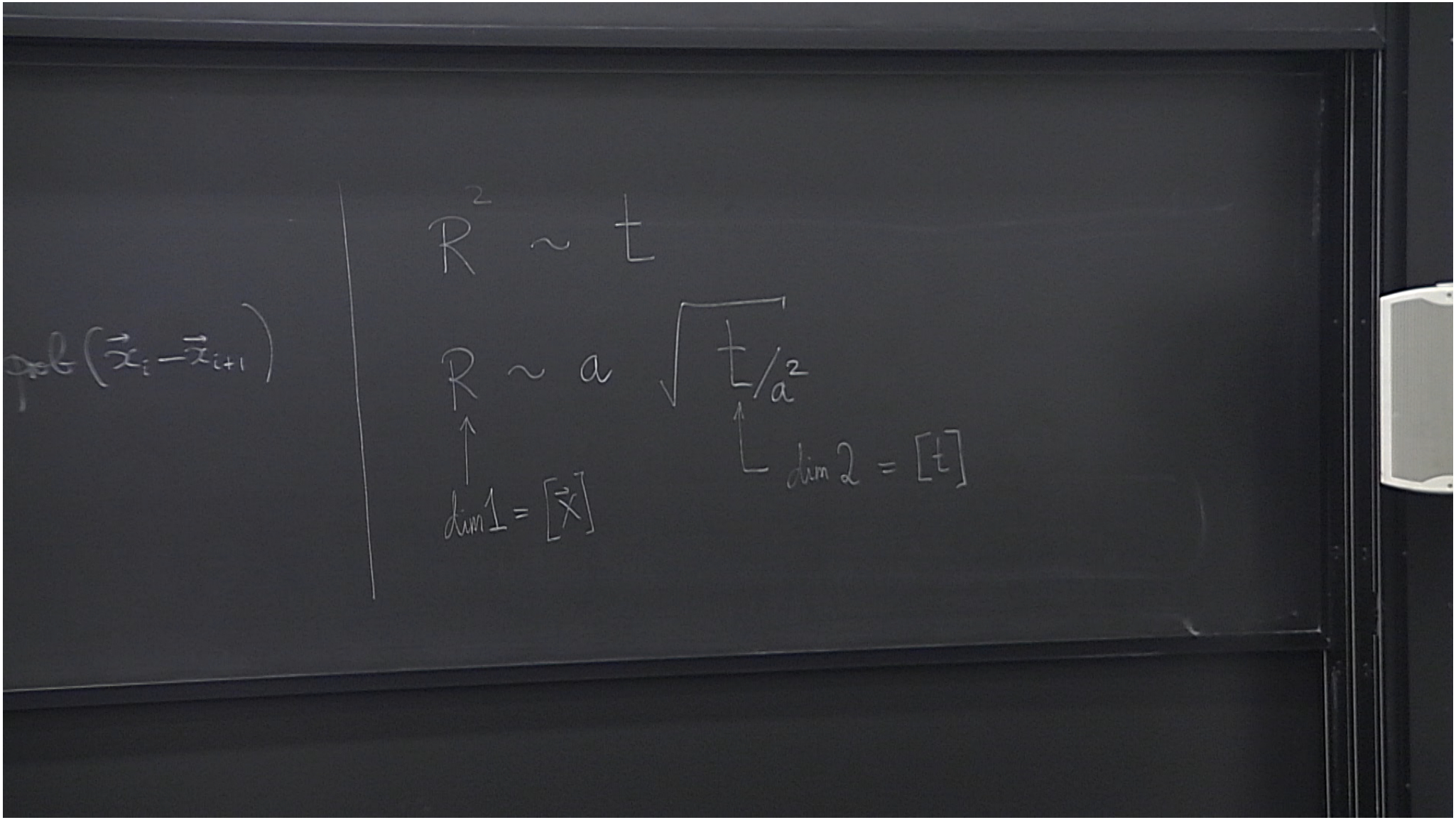

$Z' = Z^2 + 2Z^3 + Z^4$
K=Z
K'(K)
$(K_c-K)\cdot\frac{\partial K'}{\partial K}\Big|_{K_c} = (K'-K_c)$
K-K'
Z=0 Stable fixed pt, small walks
Z_c unstable critical pt
Z=∞ closed walks
unrestricted RW
biased RW
SAW
R
RG
$\tilde{Z}$
Z
$R \sim N^{\nu}$, $\frac{1}{2} < \nu < 1$
M_N = number of SAW with N steps $\sim \mu^N$
$\sum_{K'=K} \zeta(K) = 2 \sum \zeta(K')$
$\frac{1}{(K_c-K)^{\nu}} = 2 \frac{1}{\left(\frac{\partial K'}{\partial K}\right)^{\nu}(K_c-K)^{\nu}}$
$=1$
$\simeq 0.715$ $\simeq 0.75$ = exact result
not ok!
$\mu = \lim_{N\to\infty} \frac{1}{N} \log M_N \in [d, 2d-1]$
still ok
(more precisely could (is) be more like $\mu^n n^r$ or similar)

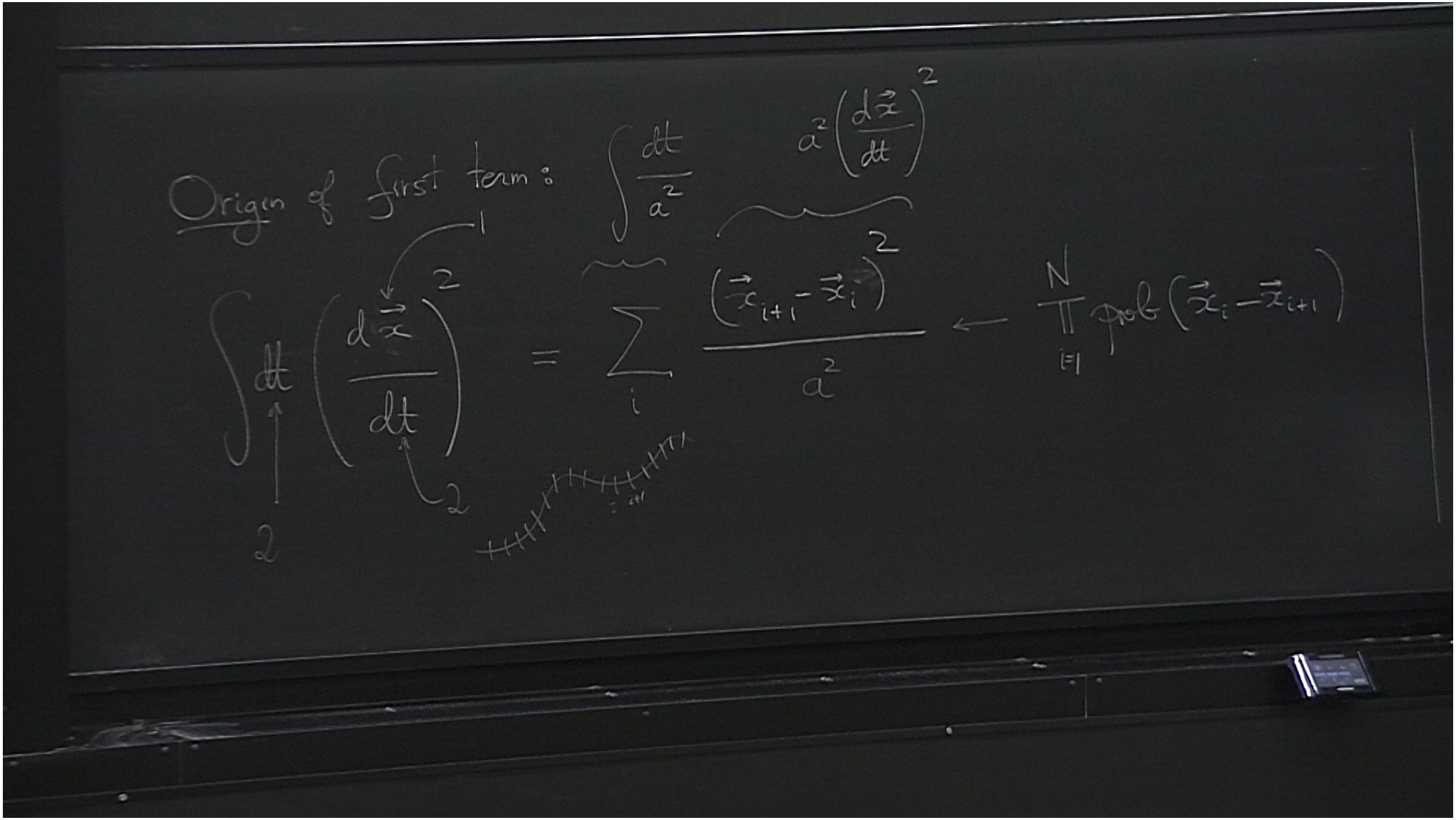

$V_{N+1} = (V_N + H_N)\,v$
$H_{N+1} = (2V_N + H_N)\,s$
$G(v,h) = G \equiv \sum_{N=1}^{\infty} (H_N + V_N)$
$G(z)$
$v = s = z$
$\sum_{\text{paths}} v^{\#\uparrow}\, s^{\#\leftrightarrow}\, 1$
(gen from $v = h = z$ then
$l = \#\uparrow + \#\leftrightarrow$
$\#\uparrow$
l
s
z
v


$v\frac{\partial}{\partial v}G = \sum_{\text{paths}} (\#\uparrow)\, v^{\#\uparrow}\, \lambda^{\#\leftrightarrow}$
$v\frac{\partial}{\partial v}\log G\Big|_{v=\lambda=z} = \sum_{\text{paths}} (\#\uparrow)\, z^{\ell} \Big/ \sum_{\text{paths}} z^{\ell} = \langle \ell \sum_{\text{paths}} \rangle$
$\left(v\frac{\partial}{\partial v} + \lambda\frac{\partial}{\partial \lambda}\right)\log G\Big|_{v=\lambda=z} = \sum_{\text{paths}} \ell\, z^{\ell} \Big/ \sum z^{\ell} = \langle \ell \rangle = \bar{N}$


SAW in the continuum.
$H[\vec{x}(t)]_{SAW} = \int dt \left(\frac{d\vec{x}}{dt}\right)^2 + u\, a^{d-4} \int dt_1 \int dt_2\, \delta^{(d)}\left(\vec{x}(t_1) - \vec{x}(t_2)\right)$
$\vec{x}(t)$
usual RW
lattice spacing
cut-off


Origin of first term:
$\int dt \left(\frac{d\vec{x}}{dt}\right)^2 = \sum_i \frac{(\vec{x}_{i+1} - \vec{x}_i)^2}{a^2} \leftarrow \prod_{i=1}^{N} \text{prob}(\vec{x}_i - \vec{x}_{i+1})$


$R^2 \sim t$
$R \sim a\sqrt{t/a^2}$
$\dim 1 = [\vec{x}]$
$\dim 2 = [t]$


Origin of first term:
$\int \frac{dt}{a^2}$
$a^2\left(\frac{d\vec{x}}{dt}\right)^2$
$\int dt \left(\frac{d\vec{x}}{dt}\right)^2 = \sum_i \frac{(\vec{x}_{i+1} - \vec{x}_i)^2}{a^2}$
$\leftarrow \prod_{i=1}^{N} prob(\vec{x}_i - \vec{x}_{i+1})$
1
2
2

SAW in the continuum.

$$H[\vec{x}(t)]_{SAW} \equiv \int dt \left(\frac{d\vec{x}}{dt}\right)^2 + u\, a^{d-4} \int dt_1 \int dt_2\, \delta^{(d)}\left(\vec{x}(t_1) - \vec{x}(t_2)\right)$$

$\vec{x}(t)$ — usual RW

lattice spacing

cut-off

repulsion to get no intersection

u dimensionless, $u=0 \rightarrow$ URW

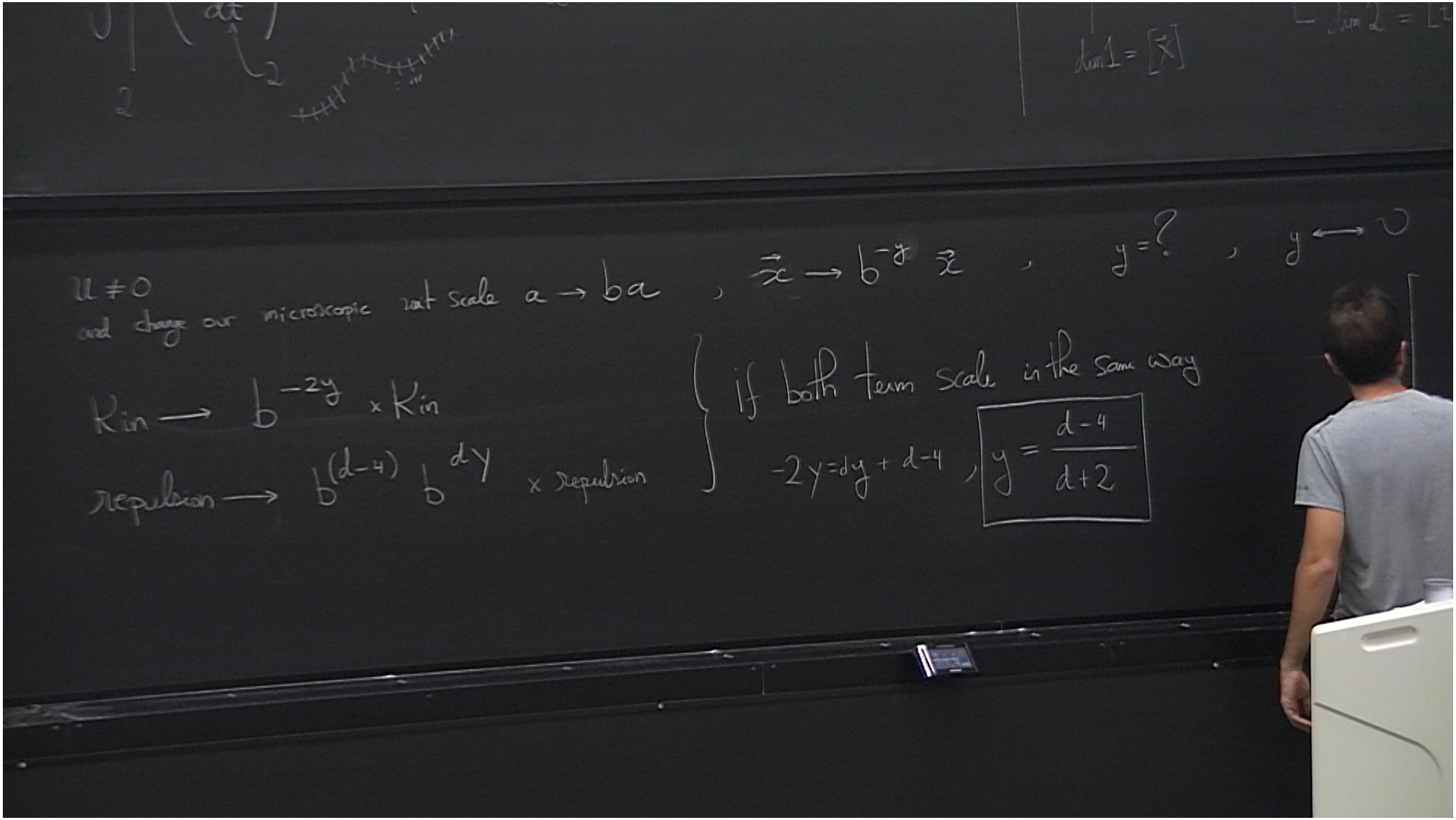
Origin of [illegible]:

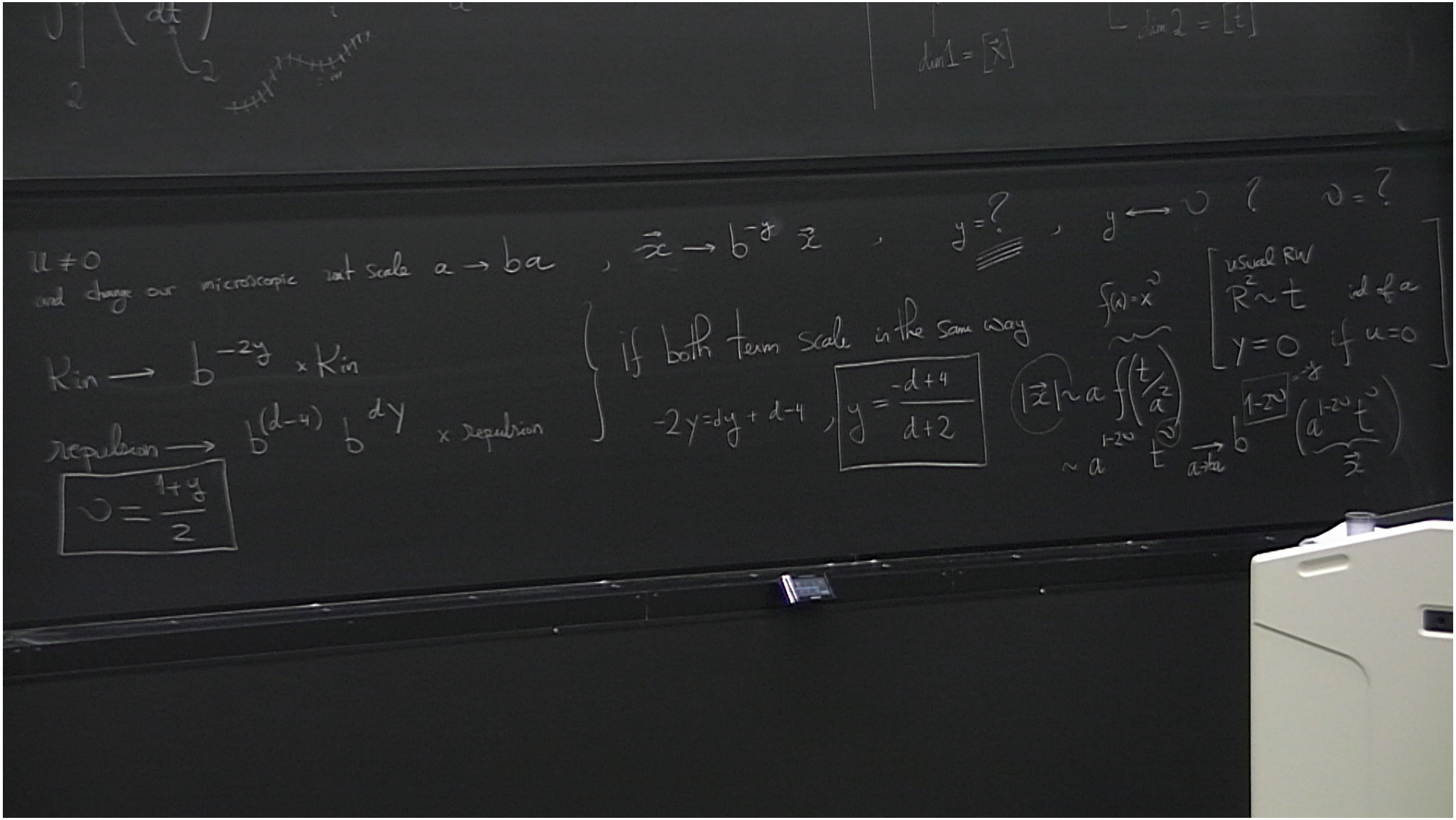
$$\frac{1}{a^2}\left(\frac{d\vec{x}}{dt}\right)^2 \sim \left(\vec{x}_{i+1} - \vec{x}_i\right)^2$$

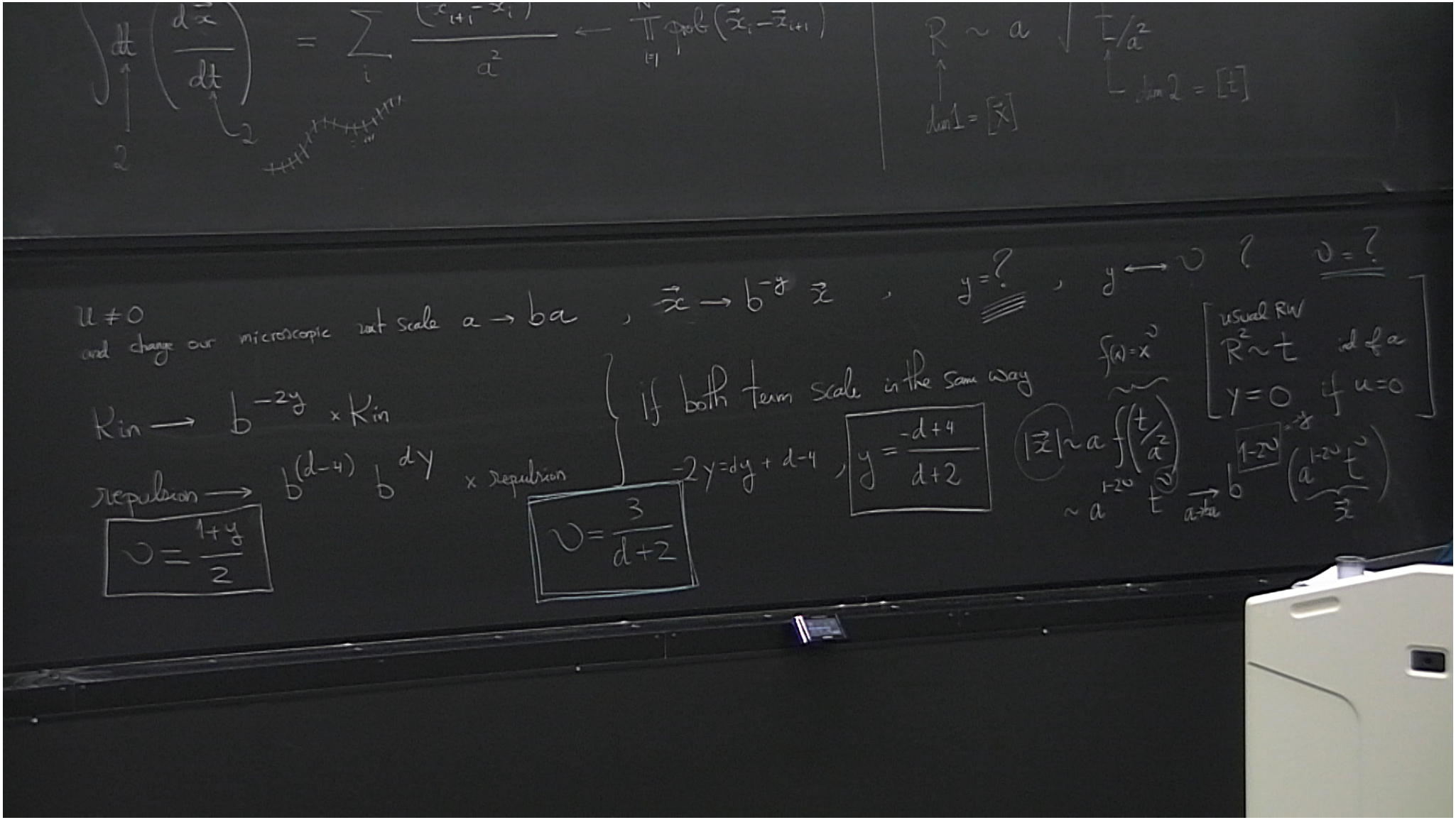
$$T \sum_{i=1}^{N} \left(\vec{x}_i - \vec{x}_{i+1}\right)$$

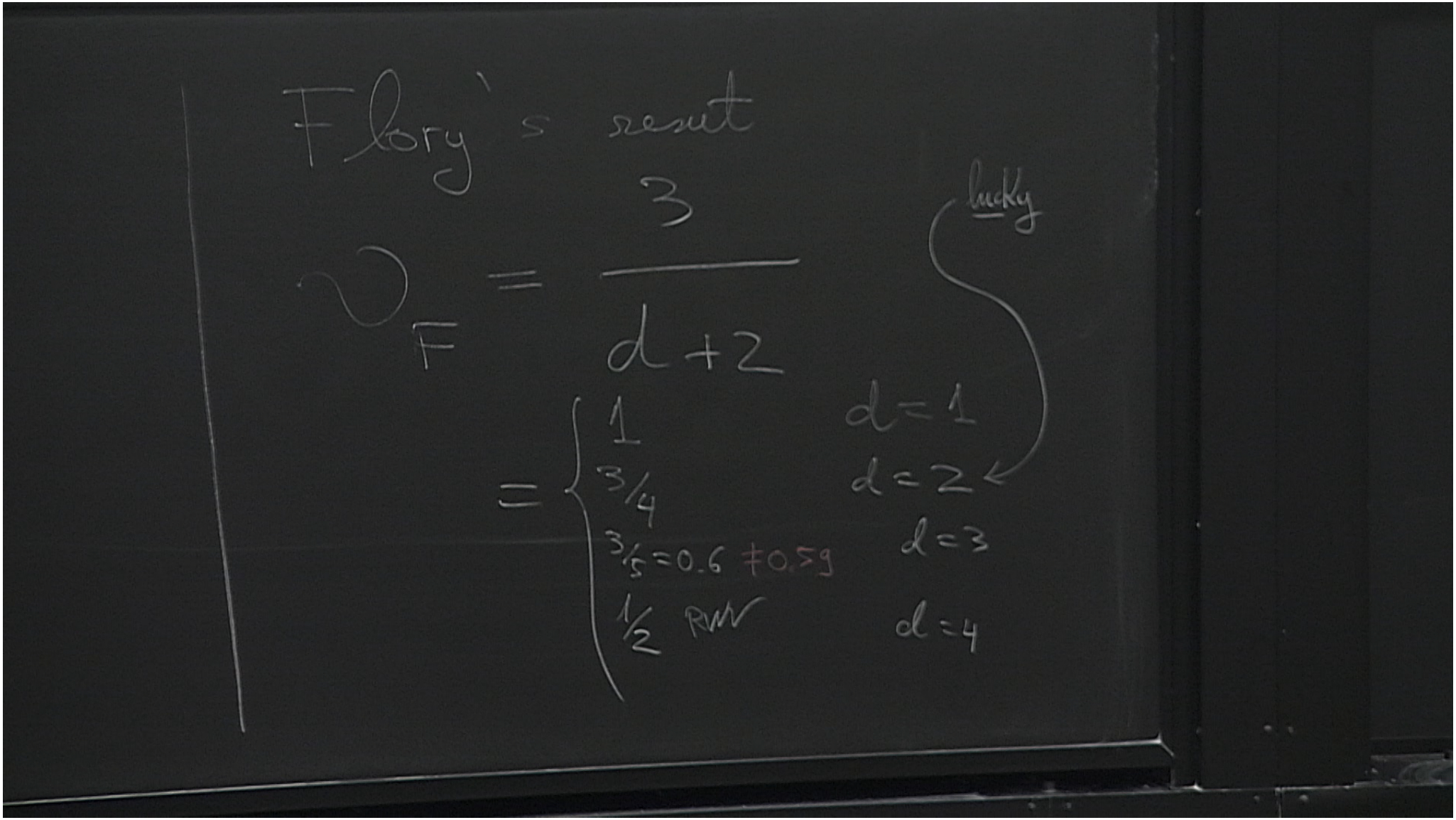
$$R^2 \sim t$$

$$R \sim a\sqrt{t/a^2}$$

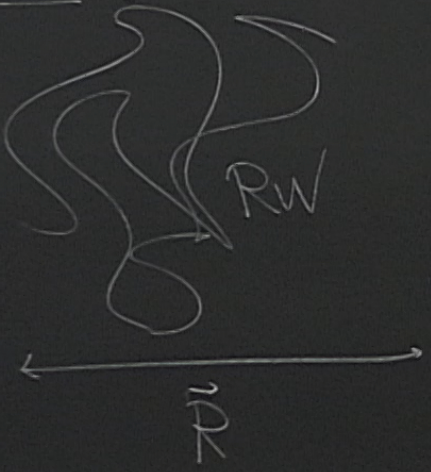

dim 1 = [x]
u ≠ 0
and change our microscopic unit scale a → ba , x → b^{-y} x , y = ? , y ⟷ v
Kin → b^{-2y} × Kin
repulsion → b^{(d-4)} b^{dy} × repulsion
{ if both term scale in the same way
-2y = dy + d - 4 , y = (d-4)/(d+2)


dim 1 = [x]
dim 2 = [t]
u ≠ 0
and change our microscopic unit scale a → ba , x → b^{-y} x , y = ? , y ↔ ν ? ν = ?
Kin → b^{-2y} × Kin
repulsion → b^{(d-4)} b^{dy} × repulsion
if both term scale in the same way
-2y = dy + d - 4 , y = (-d+4)/(d+2)
ν = (1+y)/2
f(x) = x^ν
|x| ~ a f(t/a^z)
~ a^{1-2ν} t^ν
a → ba
b^{1-2ν} (a^{1-2ν} t)^ν
usual RW
R^2 ~ t
y = 0 if u = 0


$\int dt \left(\frac{d\vec{x}}{dt}\right)^2 = \sum_i \frac{(\vec{x}_{i+1}-\vec{x}_i)^2}{a^2} \leftarrow \prod_{i=1}^{N} \text{prob}(\vec{x}_i - \vec{x}_{i+1})$
$R \sim a \sqrt{I/a^2}$
$\dim 1 = [\vec{x}]$
$\dim 2 = [I]$
$u \neq 0$
and change our microscopic unit scale $a \to ba$, $\vec{x} \to b^{-y}\vec{x}$, $y = ?$, $y \longleftrightarrow v$? $v = ?$
$Kin \longrightarrow b^{-2y} \times Kin$
$repulsion \longrightarrow b^{(d-4)}\, b^{dy} \times repulsion$
If both term scale in the same way
$-2y = dy + d - 4$, $y = \frac{-d+4}{d+2}$
$v = \frac{1+y}{2}$
$v = \frac{3}{d+2}$
$f(x) = x^v$
$|\vec{x}| \sim a f\left(\frac{t}{a^z}\right)$
$\sim a^{1-zv} t^v$
$a \to ba$
b^{1-zv}
$\left(a^{1-zv} t^v\right)$
$\vec{x}$
usual RW
$R^2 \sim t$ if a
$y = 0$ if $u = 0$


Flory's result
$\nu_F = \frac{3}{d+2}$
lucky
$= \begin{cases} 1 & d=1 \\ 3/4 & d=2 \\ 3/5 = 0.6 \neq 0.59 & d=3 \\ 1/2 \text{ RW} & d=4 \end{cases}$

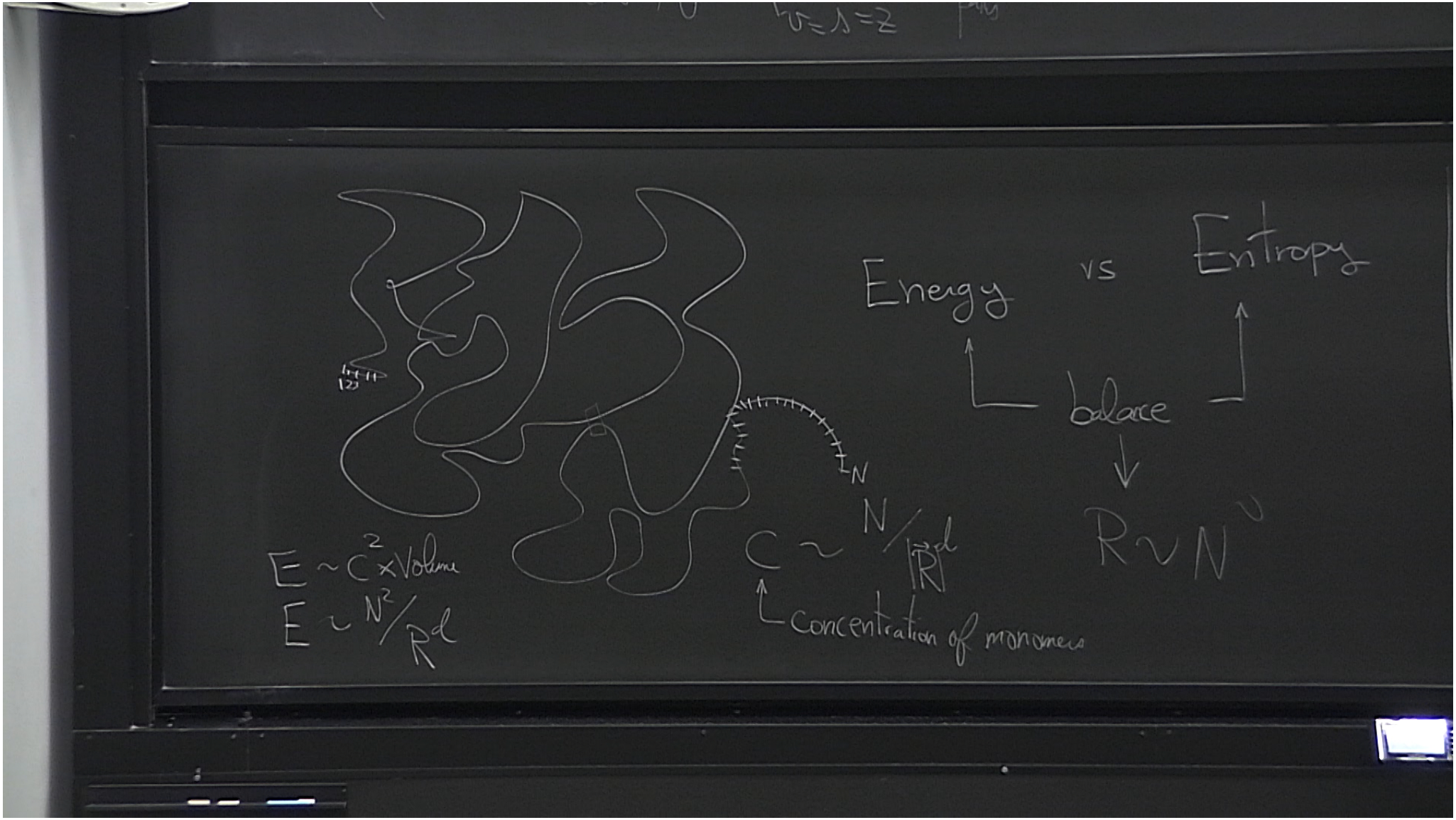
Entropy



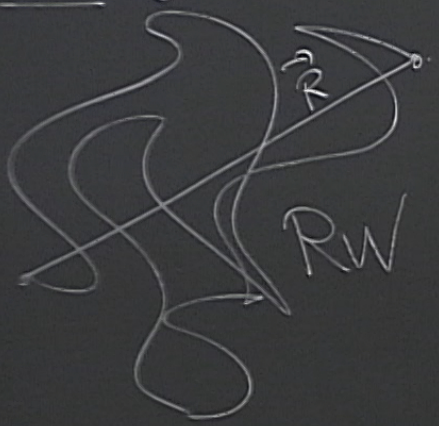
$$S(\vec{R}) = \log\left(\#_{\vec{0}\to\vec{R}} = \frac{Prob(\vec{0}\to\vec{R})}{(2q)^N}\right)$$

$e^{-q R^2}$

$$= q\vec{R}^2 + \tilde{C}$$


Energy vs Entropy
balance
$E \sim C^2 \times \text{Volume}$
$E \sim N^2/R^d$
$C \sim N/R^d$
concentration of monomers
$R \sim N^{\nu}$

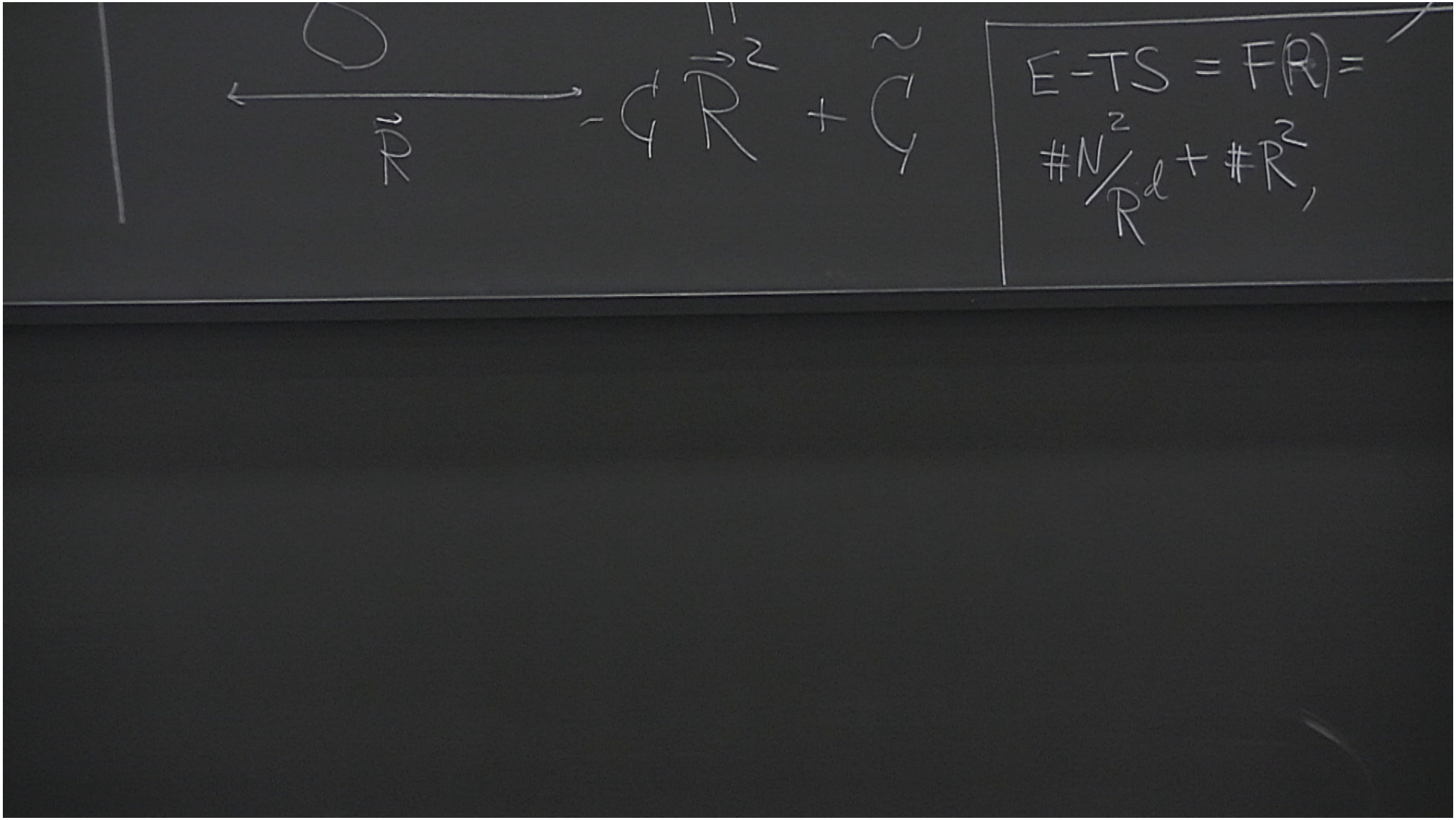
Entropy

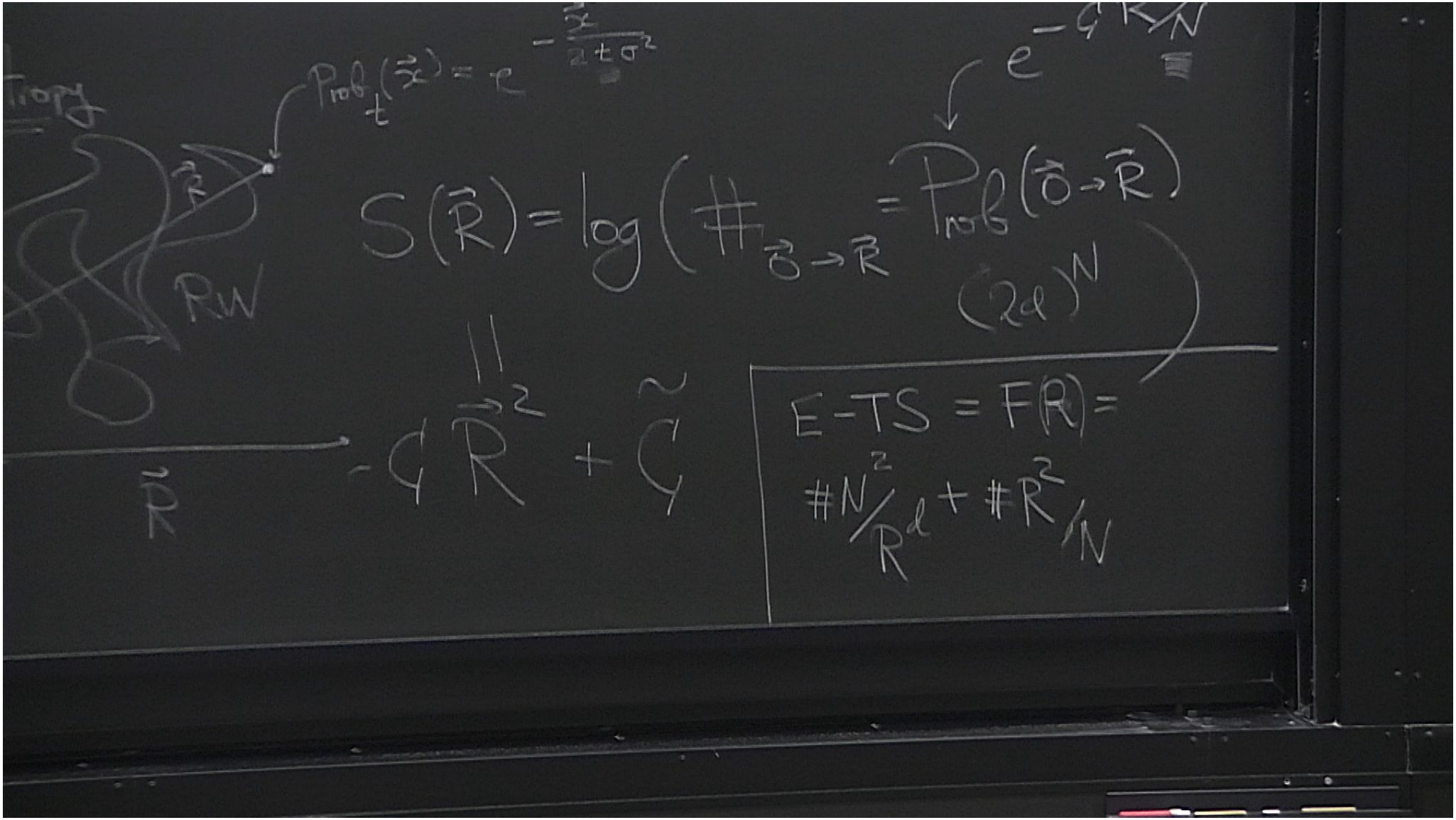


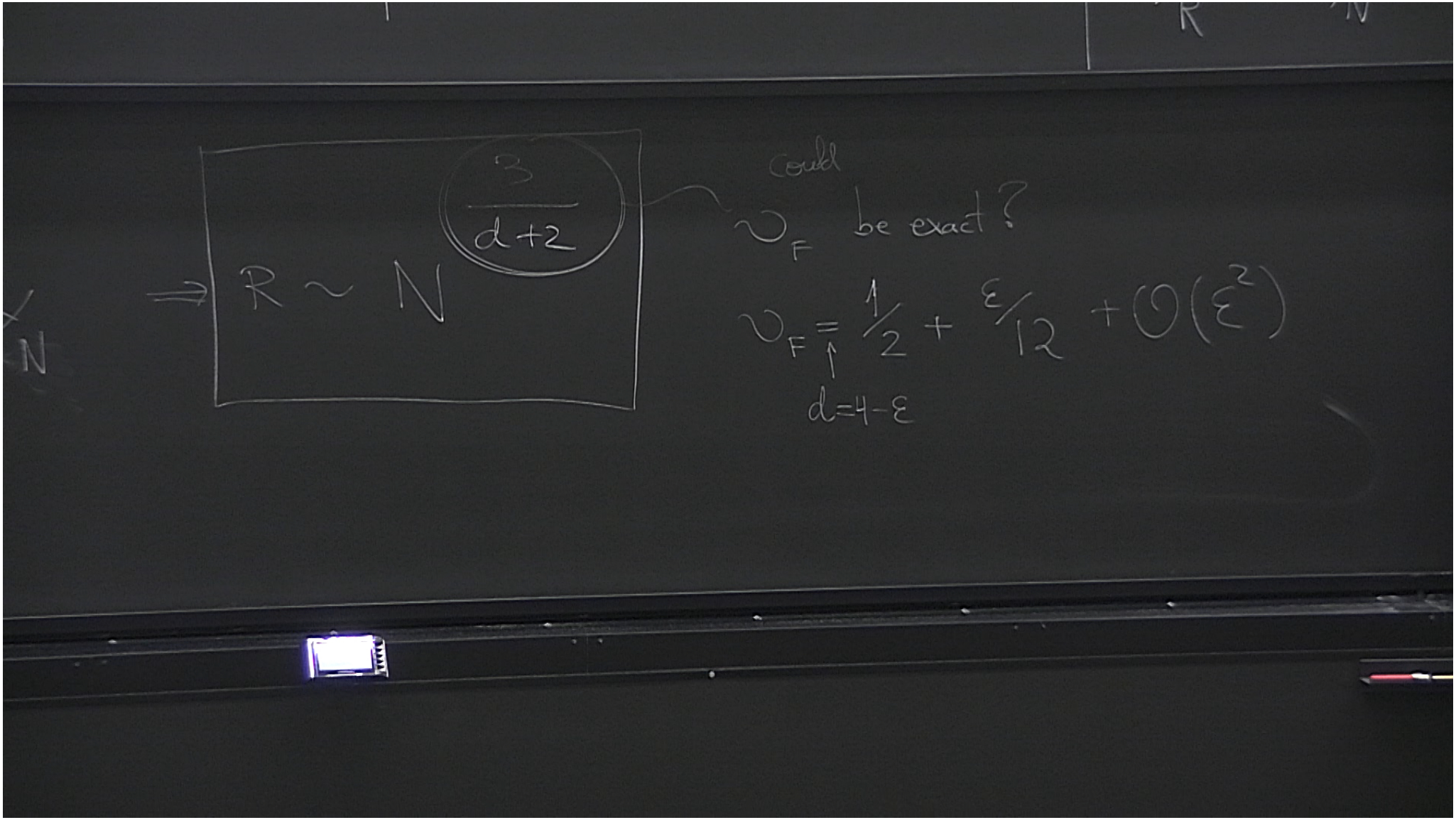
$$S(\vec{R}) = \log\left(\#_{\vec{0}\to\vec{R}}\right) = \text{Prob}(\vec{0}\to\vec{R})\,(2q)^N$$

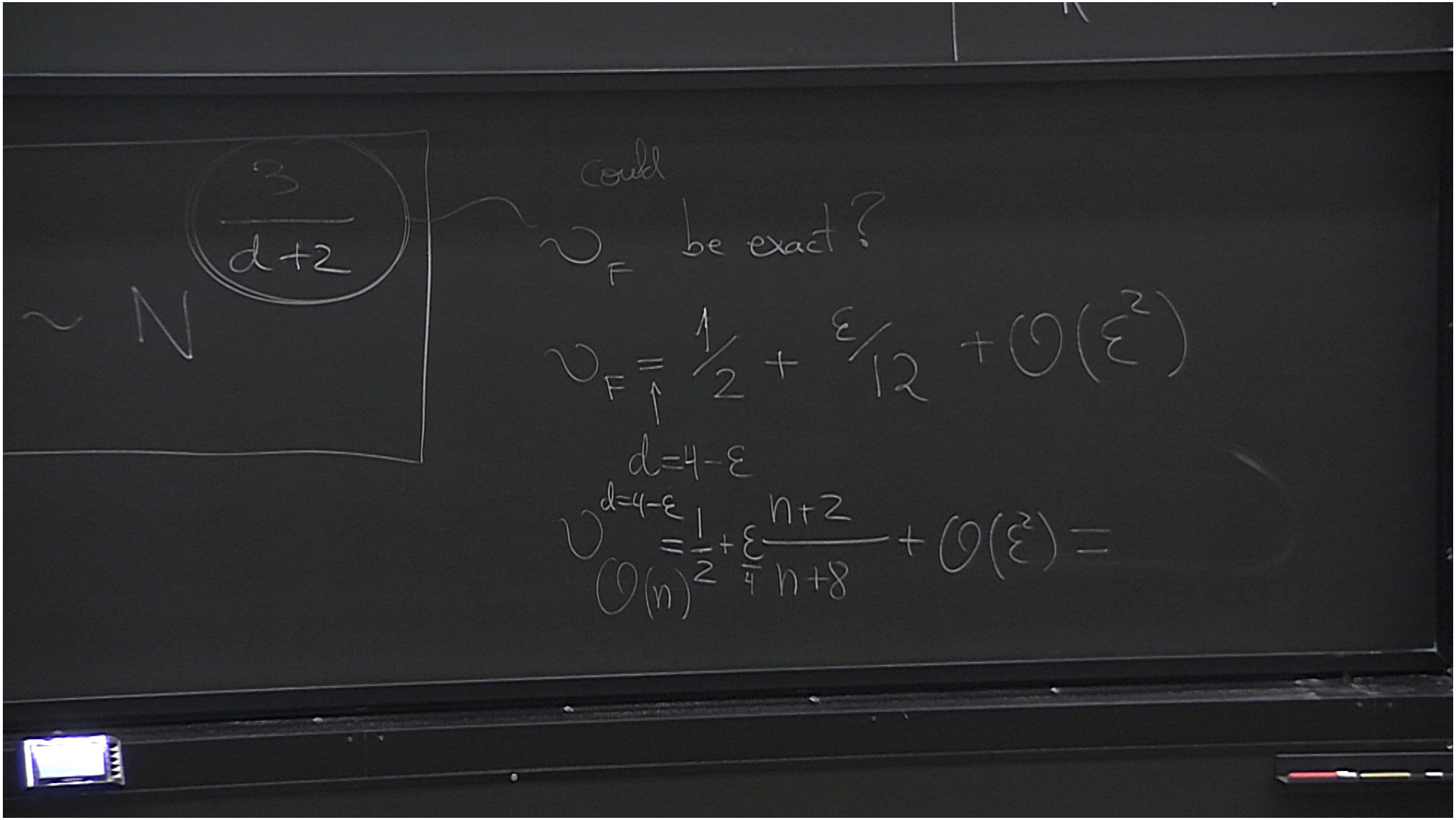
$$= -C\vec{R}^2 + \tilde{C}$$

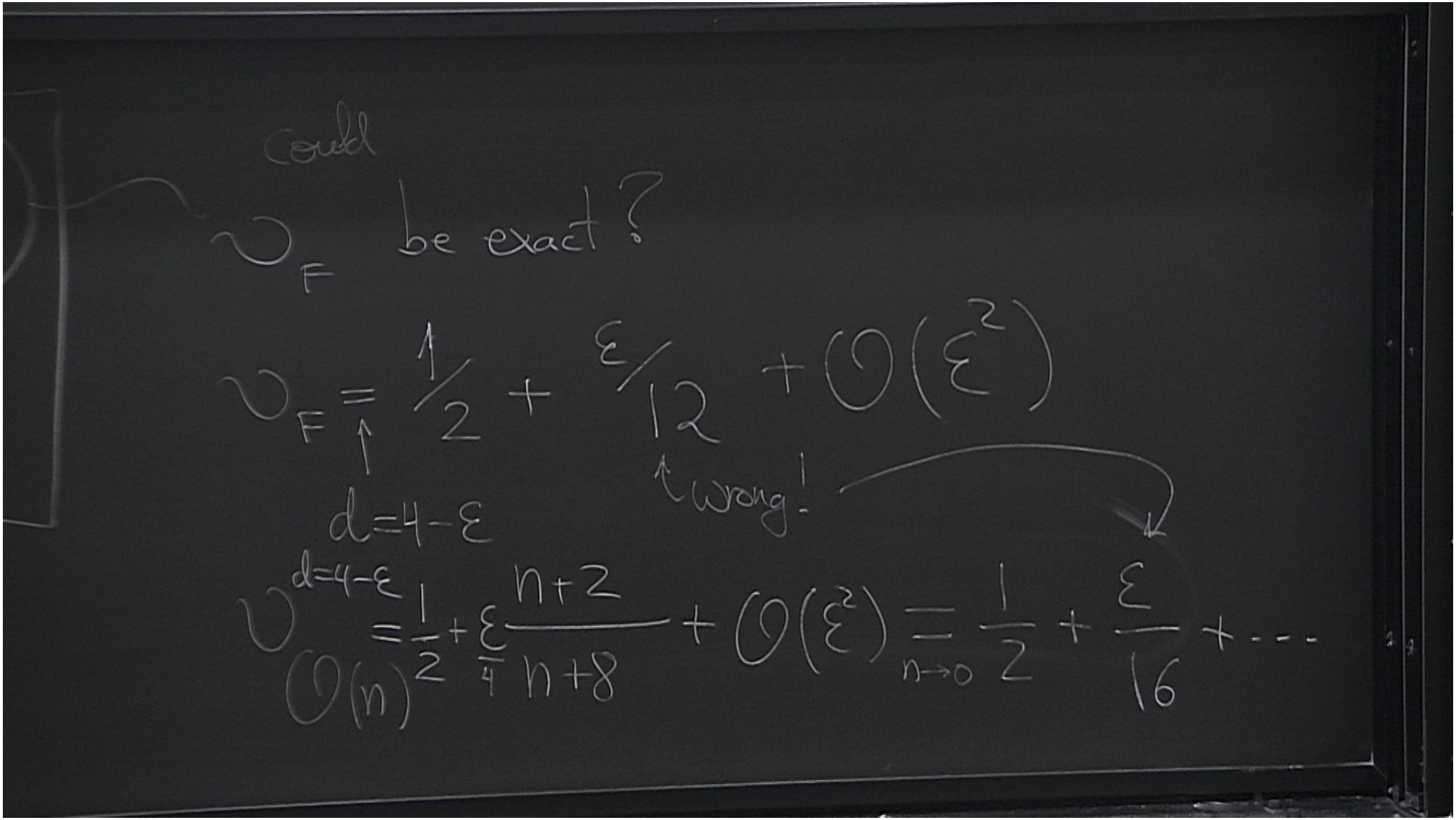
$$E - TS = F(R) = \#N/R^d + \#R^2,$$


0
$\tilde{R}$
$-C_4 \tilde{R}^2 + C_4$
$E - TS = F(R) =$
$\#N^2/R^d + \#R^2,$


Theory
RW
$\vec{R}$
$\tilde{R}$
$\text{Prob}_t(\vec{x}) = e^{-\frac{\vec{x}}{2t\sigma^2}}$
$e^{-c'R/N}$
$S(\vec{R}) = \log\left(\#_{\vec{0}\to\vec{R}} = \text{Prob}(\vec{0}\to\vec{R})\right)$
$(2d)^N$
$= -c\vec{R}^2 + \tilde{c}$
$E - TS = F(R) =$
$\#N^2/R^d + \#R^2/N$


$\Rightarrow R \sim N^{\frac{3}{d+2}}$
could
ν_F be exact?
$\nu_F = \frac{1}{2} + \frac{\varepsilon}{12} + \mathcal{O}(\varepsilon^2)$
$d = 4 - \varepsilon$


$\sim N^{\frac{3}{d+2}}$
could
ν_F be exact?
$\nu_F = \frac{1}{2} + \frac{\varepsilon}{12} + \mathcal{O}(\varepsilon^2)$
$d = 4-\varepsilon$
$\nu^{d=4-\varepsilon} = \frac{1}{2} + \varepsilon \frac{n+2}{4(n+8)} + \mathcal{O}(\varepsilon^2) =$
$\mathcal{O}(n)$


could
ν_F be exact?
$\nu_F = \frac{1}{2} + \frac{\varepsilon}{12} + \mathcal{O}(\varepsilon^2)$
wrong!
$d = 4 - \varepsilon$
$\nu^{d=4-\varepsilon} = \frac{1}{2} + \varepsilon \frac{n+2}{4(n+8)} + \mathcal{O}(\varepsilon^2) \underset{n\to 0}{=} \frac{1}{2} + \frac{\varepsilon}{16} + \dots$
$\mathcal{O}(n)$

$R \sim N$

$\frac{3}{d+2}$

Could ν_F be exact?

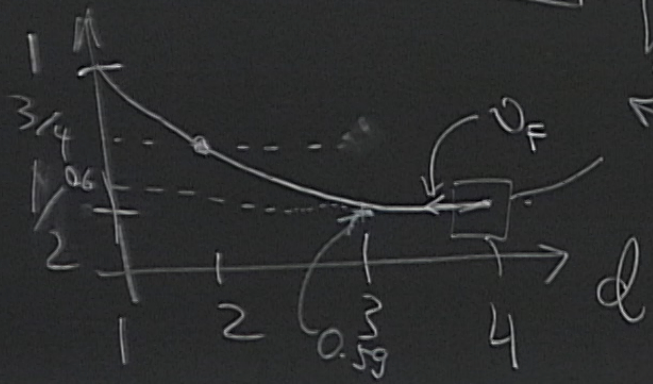
$\frac{1}{2} - \frac{\varepsilon}{12} = \nu_F = \frac{1}{2} + \frac{\varepsilon}{12} + \mathcal{O}$ ↑ wrong!

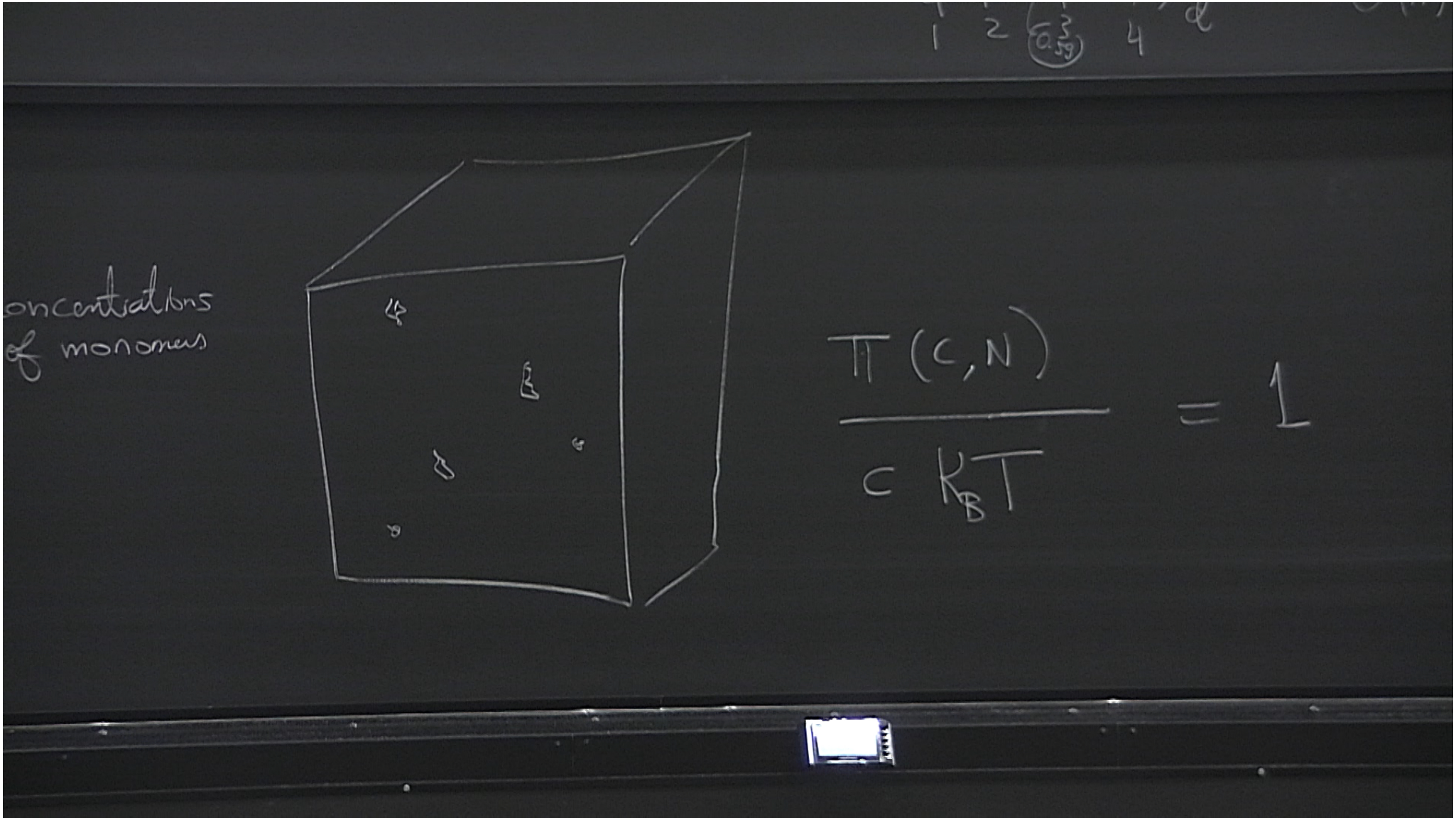
$\frac{1}{2} - \frac{\varepsilon}{16}$

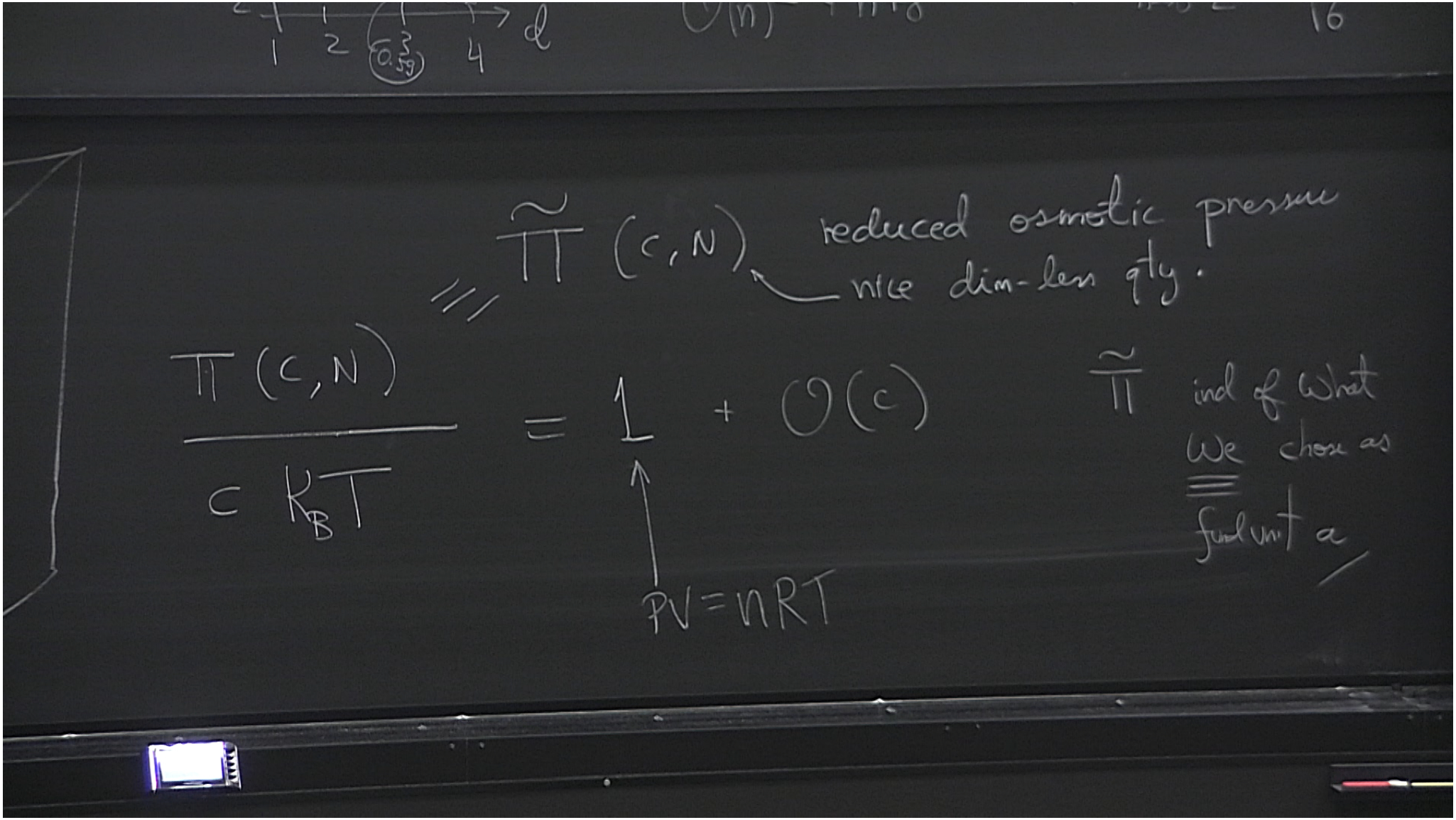
$d = 4 - \varepsilon$

$\nu^{d=4-\varepsilon} = \frac{1}{2} + \frac{\varepsilon}{4}\frac{n+2}{n+8} + \mathcal{O}(\varepsilon^2)$

$\mathcal{O}(n)$




oncentrations
of monomers
$\frac{\Pi(c,N)}{c\,k_B T} = 1$

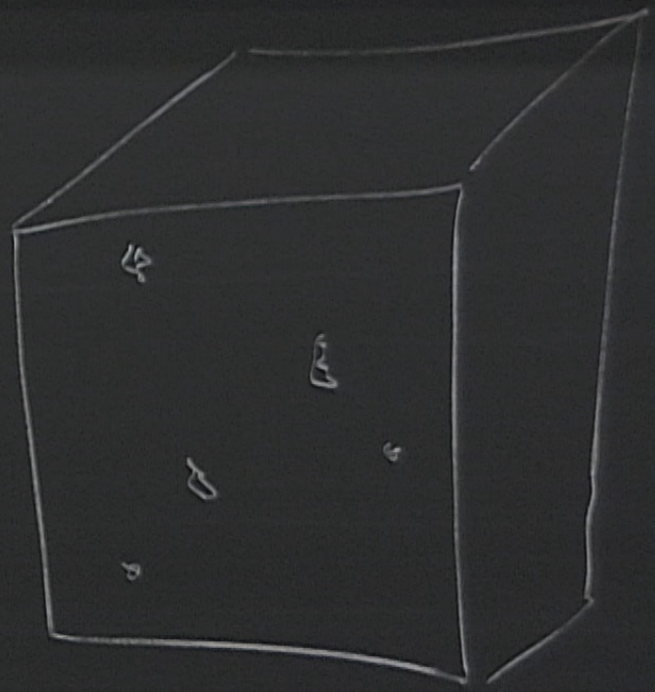

1
2
3
0.59
4
$\tilde{\Pi}(c,N)$
reduced osmotic pressure
nice dim-less qty.
$\frac{\Pi(c,N)}{c\,k_B T} = 1 + O(c)$
$\tilde{\Pi}$ ind of what we chose as fund unit a
$PV = nRT$

$C = \frac{\rho}{N}$

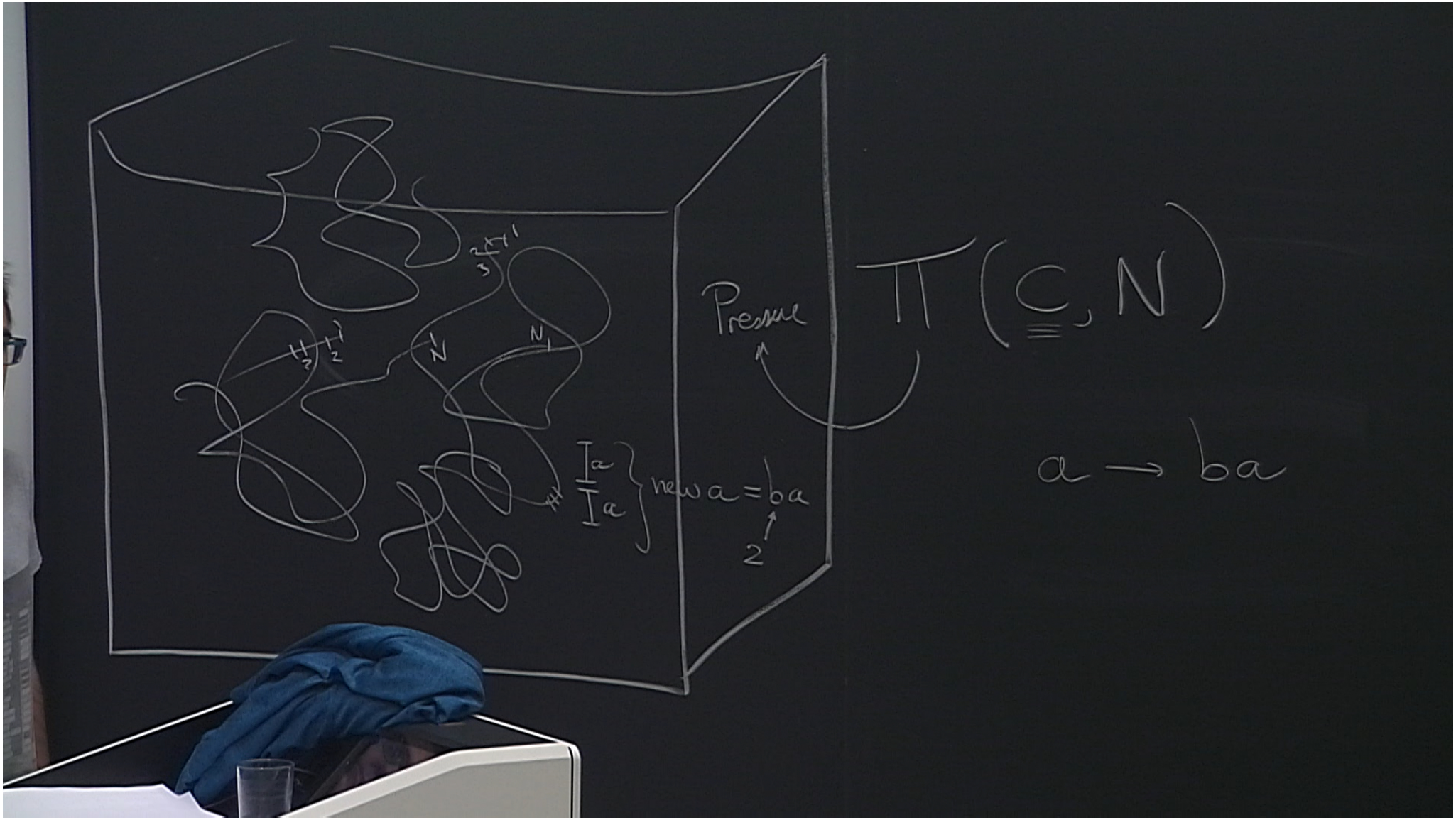
C: Concentration of polymers

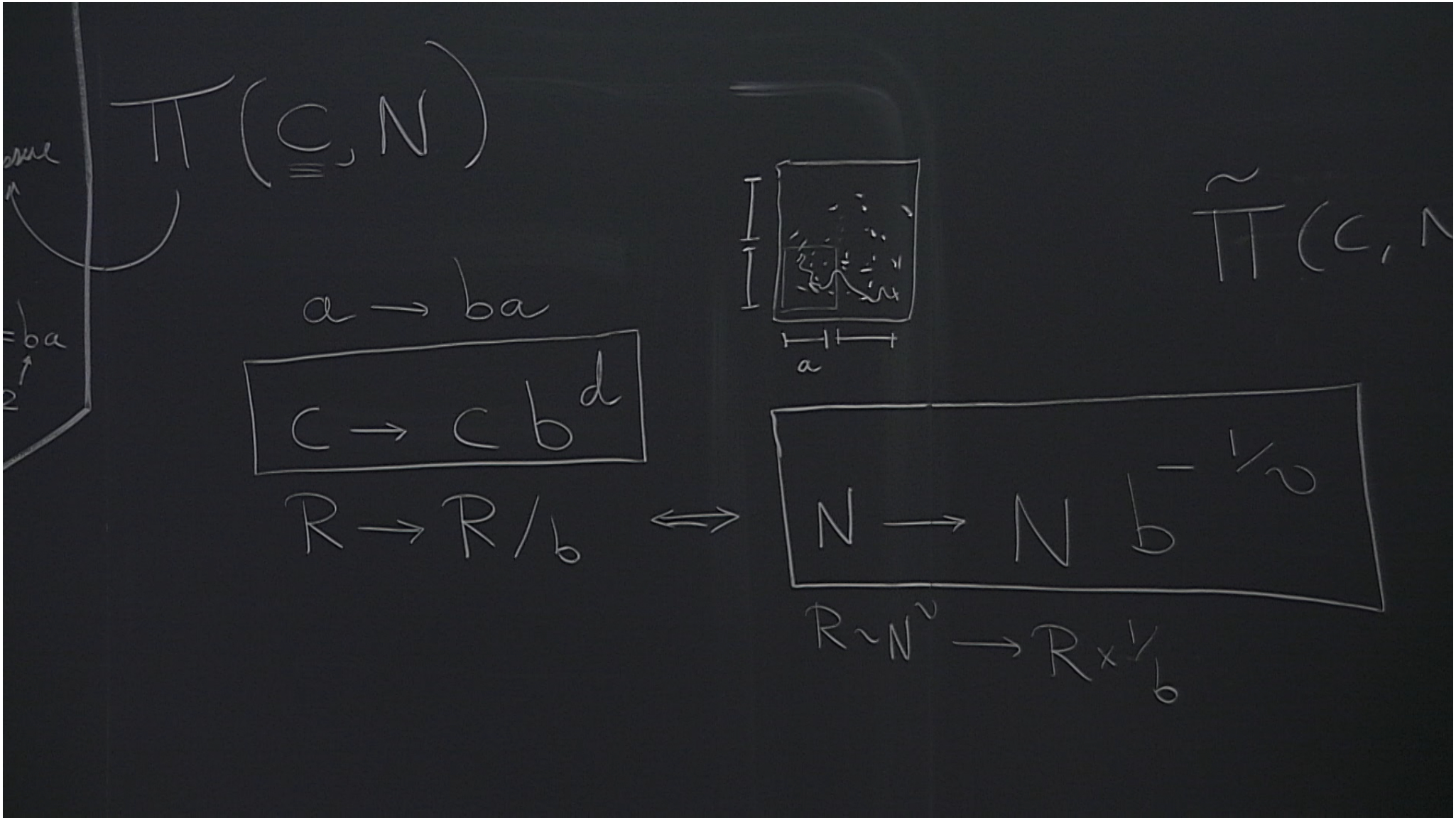
ρ: concentrations of monomers

N



$\frac{T}{C}$


Pressure
$\Pi(\underline{\underline{C}}, N)$
$a \to ba$
new $a = ba$
2


$\pi(C, N)$
$a \to ba$
$C \to C b^d$
$R \to R/b$
$\iff$
$N \to N b^{-1/2}$
$R \sim N^2 \to R \times 1/b$
a
$\tilde{\pi}(C, N$

$$\tilde{\Pi}(c, N) = \tilde{\Pi}\left(\underline{\underline{c}}\, b^{d}, \underline{\underline{N}}\, b^{-1/2}\right)$$

$$= \tilde{\Pi}\left(\frac{c\, N^{d\nu}}{c_0}\right)$$

$$N\, b^{-1/2}$$

$$R \times \frac{1}{b}$$

$$= \tilde{\Pi}\left(\underline{\underline{c}}\, b^{d}, \underline{\underline{N}}\, b^{-\frac{1}{\nu}}\right)$$

↑ ind of b

$$= \tilde{\Pi}\left(\frac{c\,N}{c_0}^{d\nu}, \mathcal{X}\right), \quad \underline{c \text{ very large}}, \; c \longrightarrow S$$

$$\Pi = c\,T\,\tilde{\Pi}\left(cN^{d\nu}\right)$$

$$= T\,\beta/N\,\tilde{\Pi}\left(\frac{\beta N}{c_0}^{d\nu-1}\right)$$

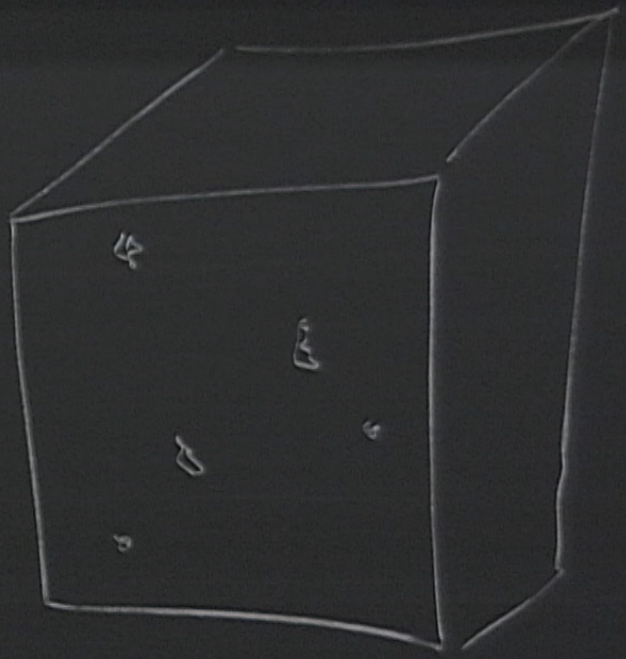
$C = \rho / N$

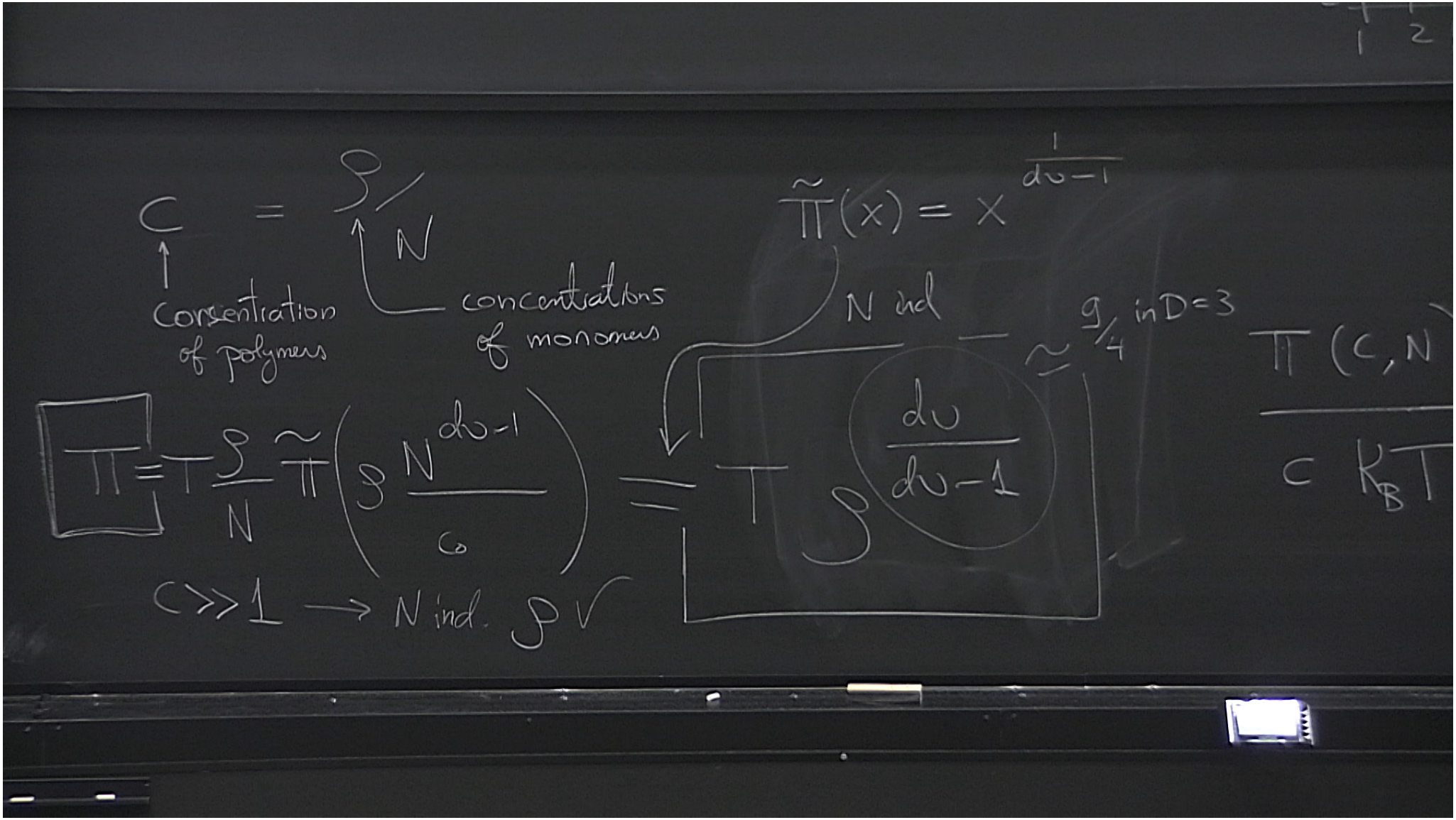
C: concentration of polymers

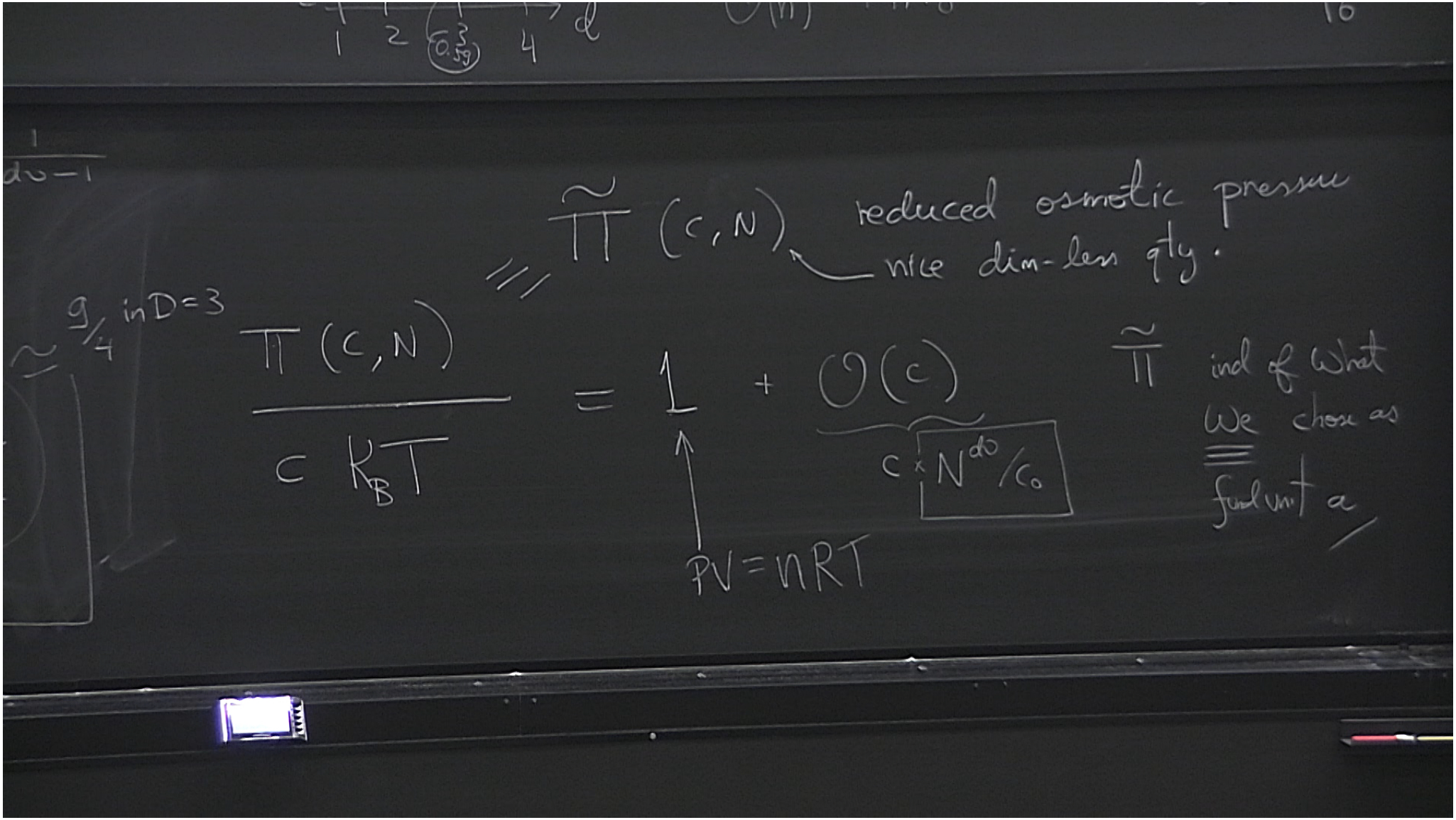
N: concentrations of monomers

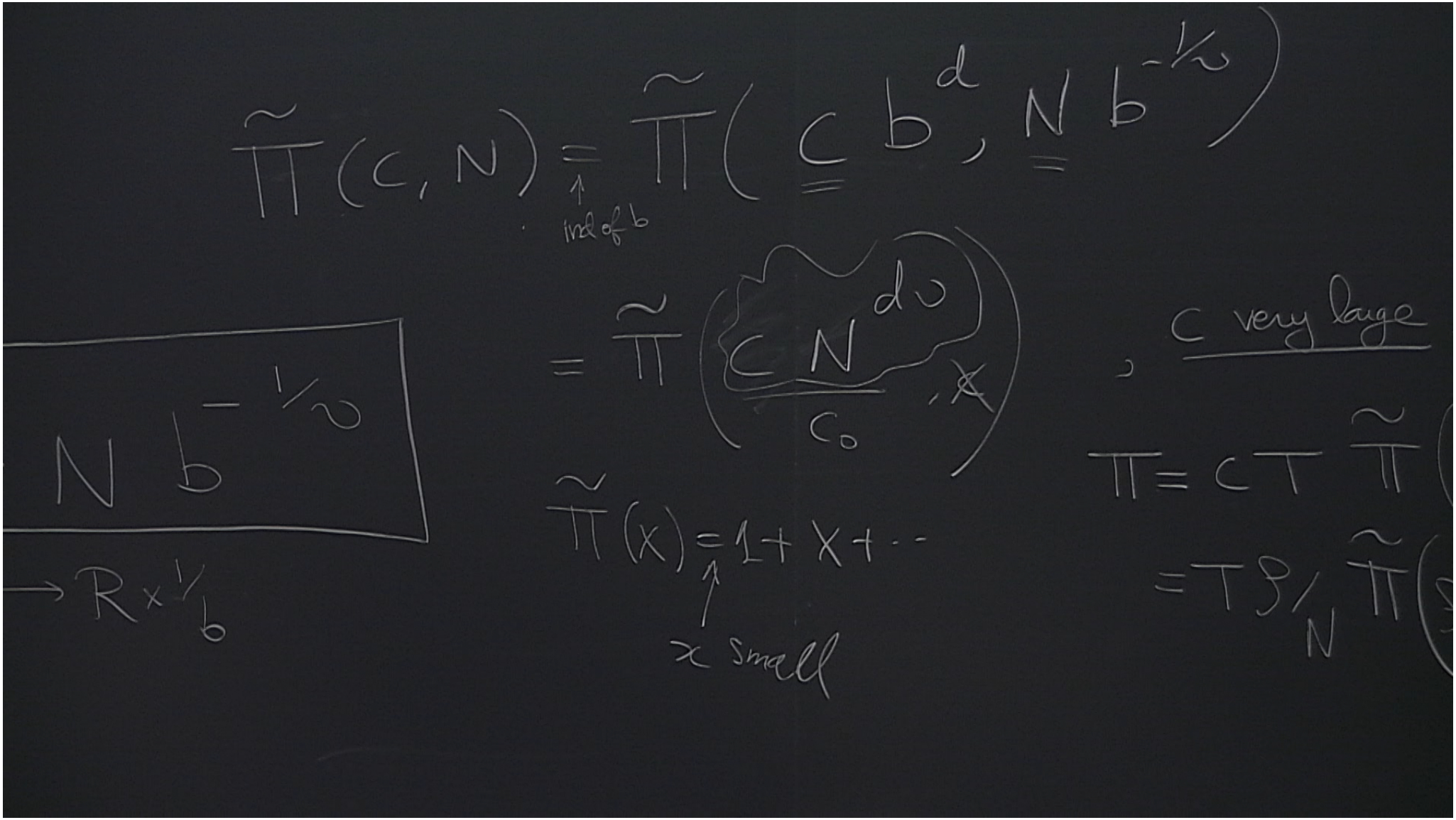
$$\Pi = T \frac{\rho}{N} \tilde{\Pi}\left(\rho \frac{N^{d\nu-1}}{c_0}\right)$$

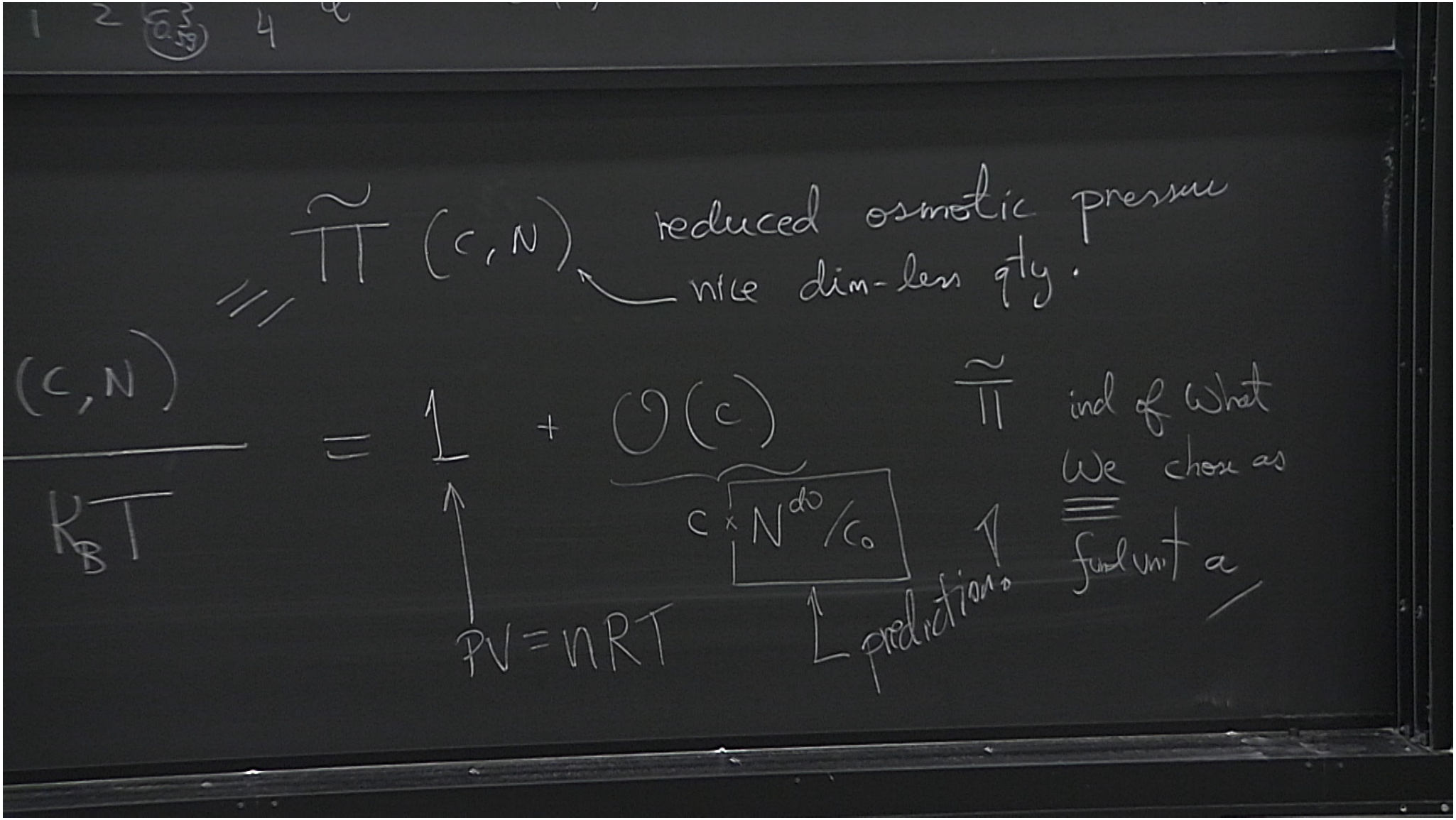
$C \gg 1 \rightarrow N$ ind. ρ ✓




c = ρ/N
Concentration of polymers
concentrations of monomers
$\tilde{\Pi}(x) = x^{\frac{1}{d\nu-1}}$
N ind
$\simeq$ g/4 in D=3
$\Pi = T\frac{\rho}{N}\tilde{\Pi}\left(\rho\frac{N^{d\nu-1}}{c}\right) = T\rho\frac{d\nu}{d\nu-1}$
$\Pi(c,N)$
$c\,k_B T$
$c \gg 1 \rightarrow$ N ind. ρ r


reduced osmotic pressure
nice dim-less qty.
$\tilde{\Pi}(c,N)$
$\frac{\Pi(c,N)}{cK_BT} = 1 + \underbrace{O(c)}_{c \times N^{d\nu}/c_0}$
$\tilde{\Pi}$ ind of what we chose as fund unit a
$PV = nRT$
$g/4$ in $D=3$
$\frac{1}{d\nu - 1}$


$\tilde{\pi}(c, N) = \tilde{\pi}(c\, b^{d}, N\, b^{-1/2})$
ind of b
$= \tilde{\pi}\left(\frac{c\, N^{d_0}}{c_0}, x\right)$
, c very large
$N\, b^{-1/2}$
$\pi = c\, T\, \tilde{\pi}$
$\tilde{\pi}(x) = 1 + x + \cdots$
$= T\, \beta_1 / N\, \tilde{\pi}$
$\to R \times 1/b$
x small


$\tilde{\Pi}(c,N)$ reduced osmotic pressure
nice dim-less qty.
$\frac{\Pi(c,N)}{K_B T} = 1 + O(c)$
$\tilde{\Pi}$ ind of what we chose as
$c \times N^{d_0}/c_0$
$\Pi V = nRT$
prediction
fund unit a