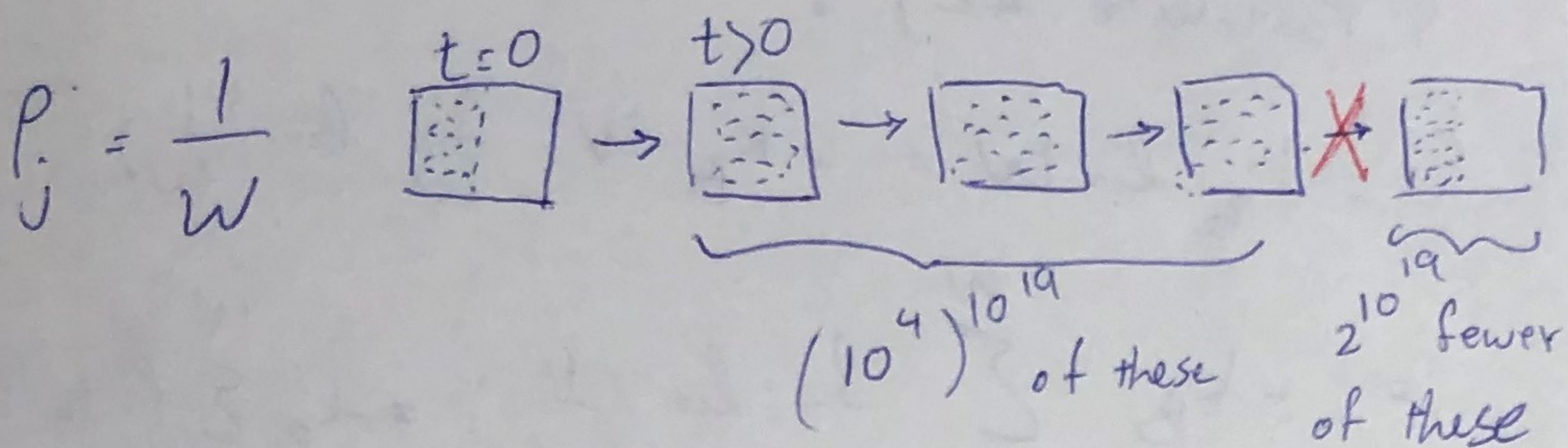


L20: review

2nd law (example wa 10^{19} molecule/cm³)



$\Rightarrow W(t > 0) \gg W(t = 0)$

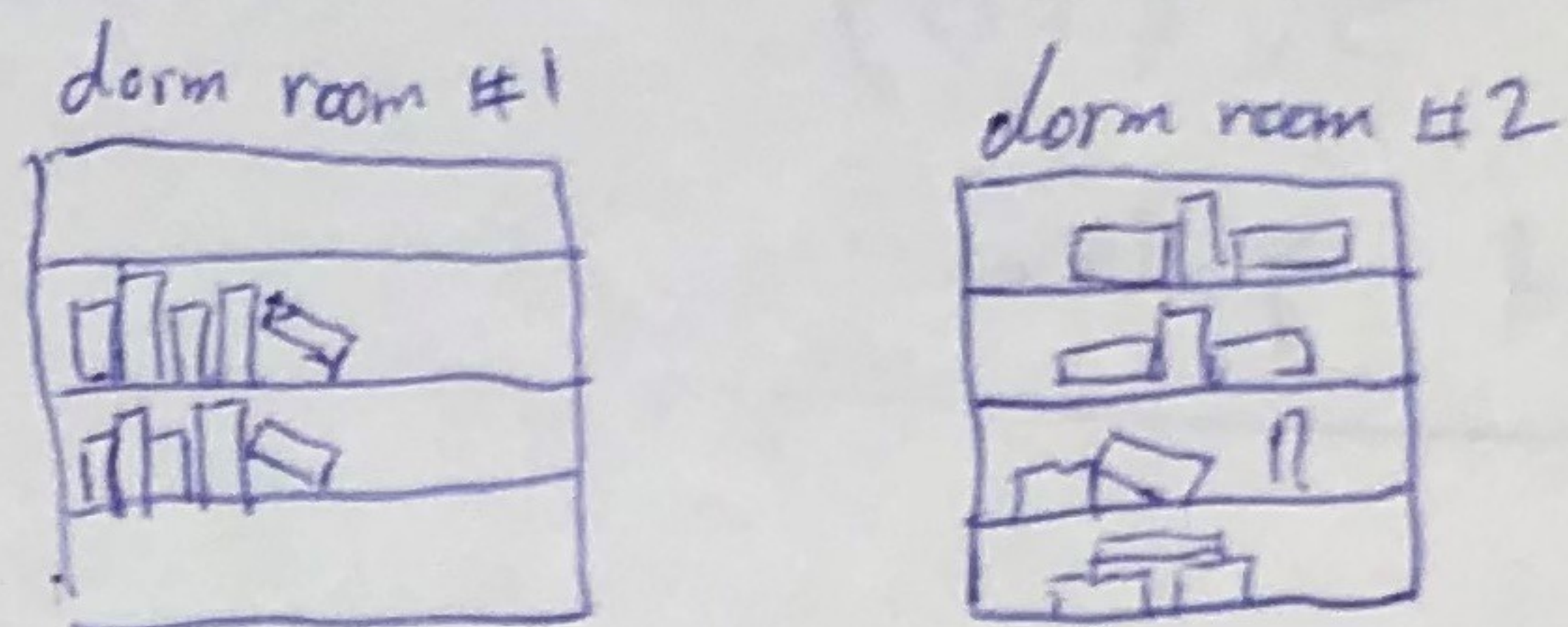
Extensive quantities:

		$E_{rot} = E_1 + E_2$
E_1	E_2	<i>extensive</i>
W_1	W_2	$W_{tot} = W_1 \cdot W_2$
		<i>multiplicative</i>
$S_1 = k_B \ln W_1$	$S_2 = k_B \ln W_2$	$S_{tot} = S_1 + S_2$
		<i>extensive</i>

k_B is the Boltzmann constant and is simply a coefficient to convert Kelvin unit to Joule unit.

Today: more about S and 3rd law

Entropy = disorder



$W_1 < W_2$

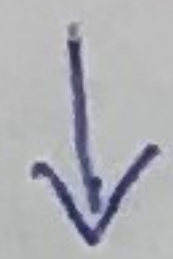
$S_1 < S_2$

Why the " k_B "?

In 19th century, it was not realized that "temperature" is "energy per degree of freedom"

$0 K \rightarrow 0 J$

$1 K \rightarrow 1.38 \times 10^{-23} J$



$S = k_B \ln W$

$\hookrightarrow 1.38 \times 10^{-23} J/K$

$S \equiv \ln W$

or, define it for a mole of particles, $R = 1.38 \times 10^{-23} \times 6.02 \times 10^{23} = 8.31 J/K \cdot mol$

$$S = R \ln W ; R = 8.31 \text{ J.mol}^{-1} \cdot \text{K}^{-1}$$

⇓

$$S(t > 0) \geq S(t = 0)$$

for isolated system

HWK S2-3

$$W \approx \left(\frac{M}{N}\right)^N = \left(\frac{V}{V_0}\right)^N \cdot N^{-N}$$

$$\Rightarrow S = k_B N \ln\left(\frac{V}{V_0}\right) - k_B N \ln N$$

entropy increases (slowly) with volume

(Entropy also increases with number of particle. Although according to the equation above S does not increase linearly with N , if we had ~~removed~~ the approximation gotten rid of

in W , entropy would have been a linear function of N)

Write entropy directly in terms of P_j

Probability of system being in microstate j

(Postulate #2):

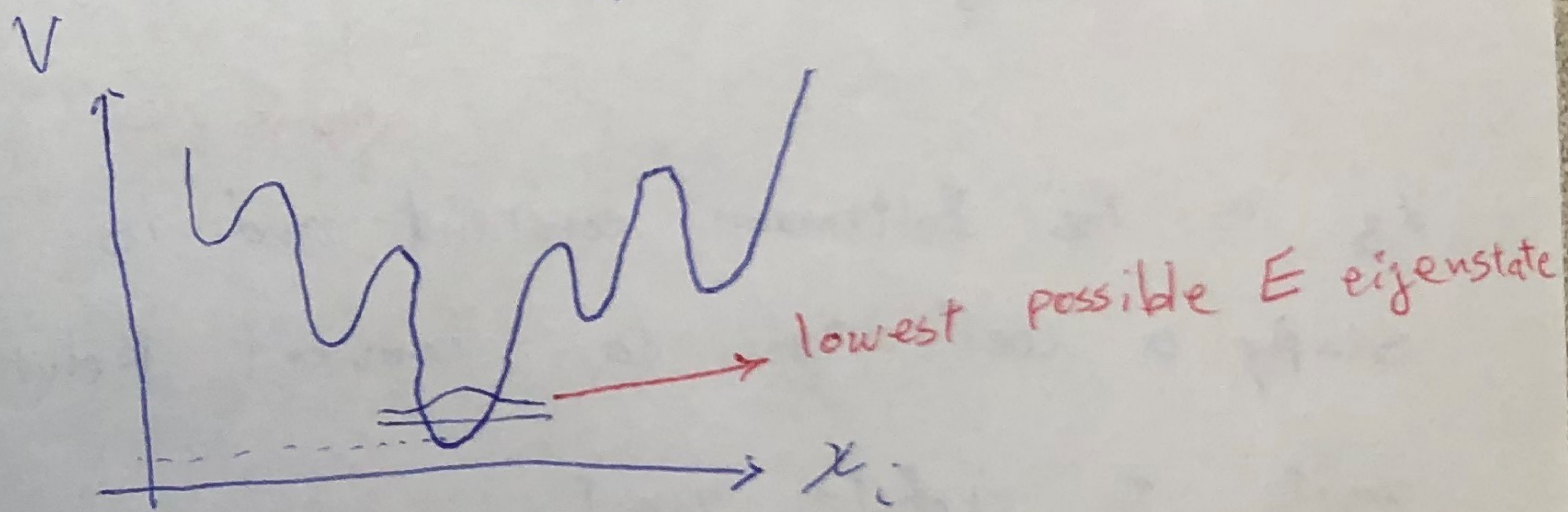
$$S = k_B \ln W = -k_B W \cdot \frac{1}{W} \ln\left(\frac{1}{W}\right)$$

$$= -k_B \sum_{j=1}^W \frac{1}{W} \ln\left(\frac{1}{W}\right) = -k_B \sum_{j=1}^W P_j \ln(P_j)$$

$$\Rightarrow \text{as } P_j \rightarrow 0, S \rightarrow \infty$$

3rd law of thermodynamics

$$H = \sum_{i=1}^N \frac{P_i^2}{2m_i} + V(x_i)$$



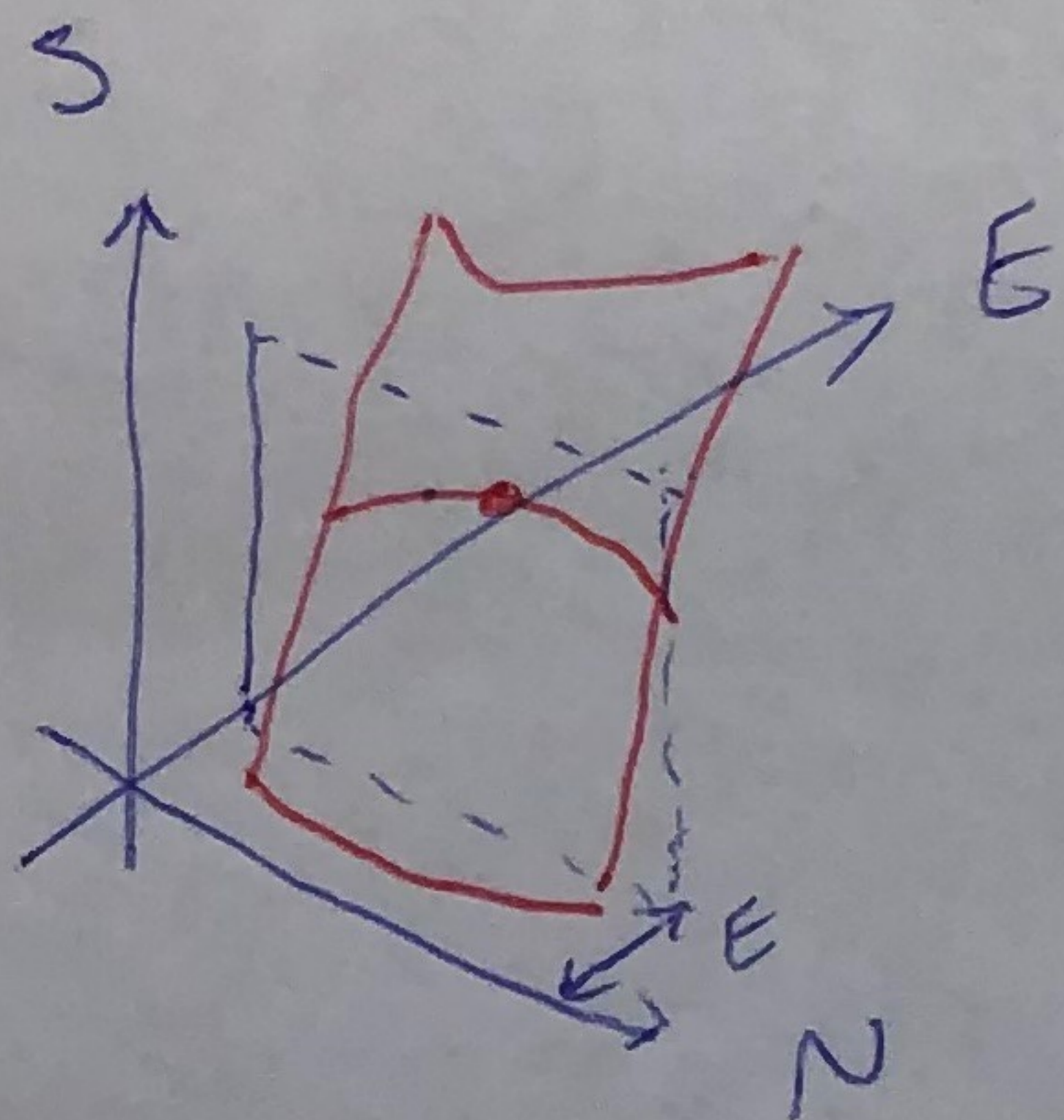
it can be proved that there is a single eigenstate for the system with minimum energy.

$$\lim_{E \rightarrow \min} W = 1 \Rightarrow \boxed{\lim_{E \rightarrow \min} S = 0} \quad (\text{because } k_B \ln(1) = 0)$$

3rd law of thermodynamics

* Simply cooling the system to zero Kelvin does not always bring entropy to zero. For materials such as window glass the kinetics of molecular rearrangement is so slow that system will get trapped in a high energy, high entropy state.

As E increases, more microstates are available $\Rightarrow W$ increases $\Rightarrow S$ increases



$S(E, N, V, \dots)$
is maximized
for isolated system

* We will see later that for systems that are not isolated, if T and P are constant, a different function (called $-G$) is maximized.