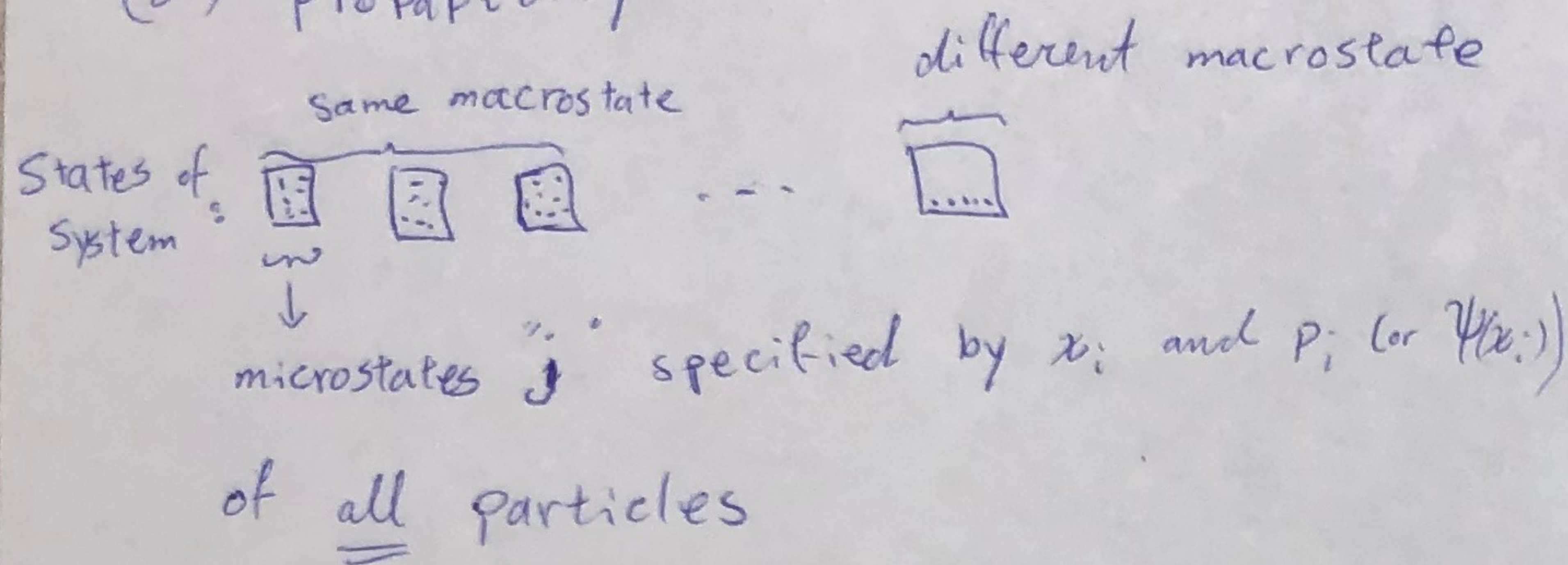


L18: review

(1) level of detail

(2) probability



\* macrostates are specified by "state functions"  $E$  (energy),  $N$  (particle numbers),  $V$  (volume), color ... that we can monitor.

\*  $P_j$ : probability of being in microstate  $j$  (or  $P(x, p)$  or  $\psi(x)$  for continuous system)

<sup>"rho"</sup> ↙

(Prof. Gruebele showed a molecular dynamics demo to illustrate microstate/macrostates of a simple system.)

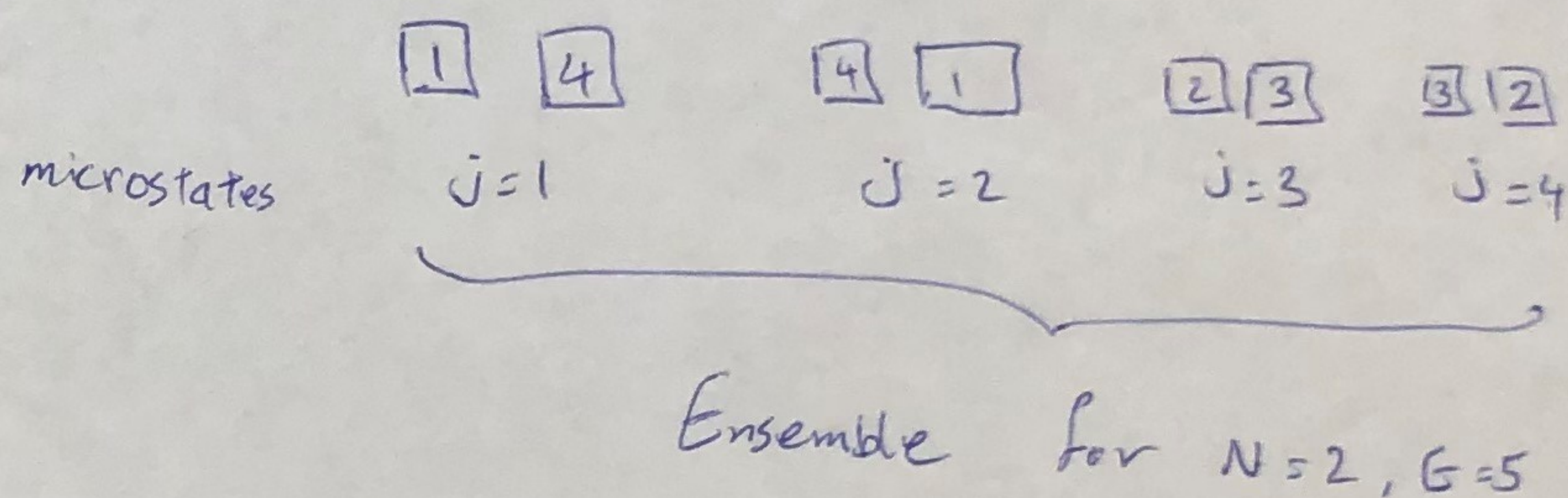
Today: Postulates of Stat Mech

Example system:  $N$  dice, macrostate given by "roll total" =  $E$  (think of each die as a molecule and its value 1-6 as its energy)

Definitions:

\* Ensemble: collection of all the microstates in a macrostate

example:  $N = 2, E = 5$



\* Partition function: Number of microstates accessible to a macrostate.

example:  $N=2, E=5$

$W = 4$  ;  $w$ : partition function

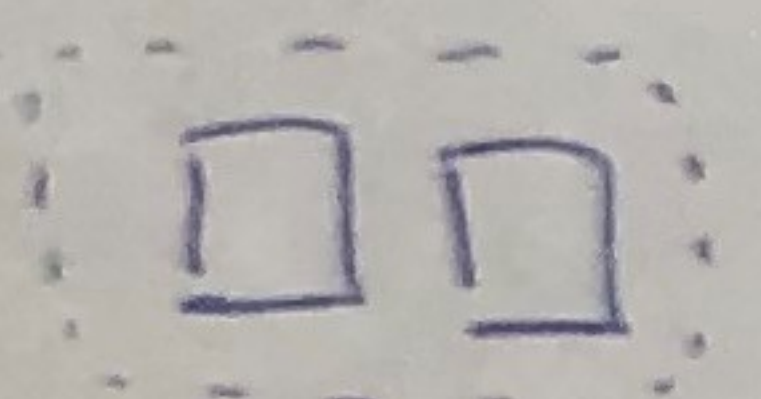


\* Extensive State Function: increases linearly with system size.

\* Intensive State Function: independent of system size.

□ ex: average total  $E$

↓ duplicate



new system with twice the size

rolled =  $N \times 3.5$   
(extensive)

average roll per die = 3.5  
(intensive)

Goal: given a system, be able to calculate the average value of any observable  $A$  (or operator  $\hat{A}$ )

Postulates

postulate #1: microscopic laws ( $F=ma, \hat{H}\psi = E\psi$ )

can be extended to very large number of particles for isolated systems specified by their state functions  $E, N \dots$

\* note that postulate #1 holds for isolated systems  $\Rightarrow$  Energy (among other state functions) is conserved.

instead of  $N$ , we'll use  $n = \frac{N}{6.02214076 \times 10^{23}}$

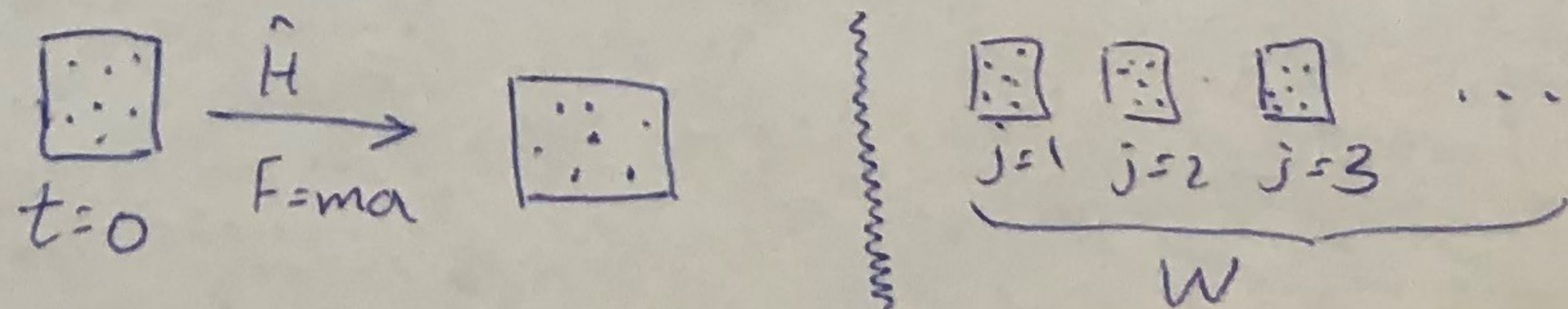
(In 2018 the base standard changed for mole and Avogadro's number; 6.02214076 is an exact number with no approximation  $\Rightarrow$  12g is the  $6.02214076 \times 10^{23}$  mass of  $^{12}\text{C}$  atoms.)

\* if ~~one~~ one die is fair, 1 mole of die is also fair

Postulate #2: Principle of equal probability

(i) "weak form": All  $W$  microstates of a system in postulate #1 ( $E = \text{const} \dots$ ) have the same probability:  $P_j = \frac{1}{W}$

(ii) "strong form": the time average is equal to the ensemble average.





\* the 'strong form' of postulate #2 is not always true: for a material such as glass, the molecules move in an extremely small space so by sampling a relatively short amount of time the averages of quantities obtained will be different from the Ensemble average.

Averaging:

$$A = \langle A \rangle = \bar{A} = \sum_{i=1}^W p_i A_i$$

$$\text{or } A(x, p) = \langle A \rangle \Rightarrow A = \iint dx dp f(x, p) A(x, p) \\ = \int dx \psi(x) A \psi^*(x)$$