3.020 Lecture 27

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1 Microstates and macrostates

Microstate (μstate): Description of the state of every molecule in a system

e.g. $O(10^{23})$ pairs of position and velocity (r, v)

- Macrostate: Description of system on macroscopic length scale, averaging over microscopic (e.g. molecular) processes.
 e.g. P, T, N
- Simple example, after DeHoff 4 particles: a, b, c, d 2 possible staes for each particles: 1, 2

- General case: n particles distributed over r states $\Omega = \#$ of microstates in the macrostate defined as :
 - $-n_1$ particles in state 1
 - $-n_2$ particles in state 2
 - n_i describes the macrostate _____

occupation numbers

$$\Omega = \frac{n!}{n_1! \; n_2! \; n_3! \; \dots \; n_r!}$$

Work this out

• For large systems :

$$n >> 1, \qquad r >> n$$

 Ω is very sharply peaked around some macrostate



• Define (i.e. count) macrostates for n particles in r states or "boxes"

index	{n;}	
١	n, 0, 0, 0, 0,	2 (r) of these
2	0, 0, 0, 0, 0,	(1) or mese
:	:	
;	n-1, 1, 0, 0, 0,	} (5) of these
1	n-1,0,1,0,0,	(~ /
	1	
		$\left(\begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array} \right)$

• We now know how to define macrostaes n_i and count them, and we now how to count microstates for each macrostate n_i

∜

Can plot distribution $\log \Omega$

2 Ergodic principle: All microstates that are compatible with constraints are equally likely

- Ensembles of μ states that all satisfy given constraints
- Time average = ensemble average
- Frequentist approach to probability and statistics
- Likelihood of finding a given macrostate is proportional to its # of microstates

$$\rho_j = \frac{\Omega_j}{\sum_k \Omega_k}$$

 ρ_j : prob. of finding macrostate j Ω_j : # of microstates in j $\sum_k \Omega_k$: total # of microstates possible within constraints Q. For what types of cases might the ergodic principle break down ? 3.020 Thermodynamics of Materials Spring 2021

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