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 states for each particles: 1, 2

  ![Diagram showing all possible microstates and macrostates]

- General case: n particles distributed over r states
  \[ \Omega = \# \text{ of microstates in the macrostate defined as :} \]
  - \( n_1 \) particles in state 1
  - \( n_2 \) particles in state 2
  - \( n_i \) describes the macrostate
\[ \Omega = \frac{n!}{n_1! \, n_2! \, n_3! \ldots \, n_r!} \]

- For large systems:

\[ n \gg 1, \quad r \gg n \]

\( \Omega \) is very sharply peaked around some macrostate

- Define (i.e. count) macrostates for \( n \) particles in \( r \) states or “boxes”

<table>
<thead>
<tr>
<th>index</th>
<th>( {n_i} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( n, 0, 0, 0, 0, \ldots )</td>
</tr>
<tr>
<td>2</td>
<td>( 0, n, 0, 0, 0, \ldots )</td>
</tr>
<tr>
<td>\vdots</td>
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\( (r) \) of these

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\( \binom{r}{\min(r, n)} \)

Challenge: Work this out!
• We now know how to define macrostates \( n_i \) and count them, and we now how to count microstates for each macrostate \( n_i \).

\[ \downarrow \]

Can plot distribution \( \log \Omega \).

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

• Ensembles of \( \mu \) 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

\[
\rho_j = \frac{\Omega_j}{\sum_k \Omega_k}
\]

\( \rho_j \): prob. of finding macrostate \( j \)
\( \Omega_j \): \# 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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