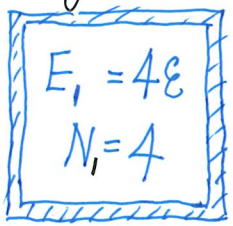
J. Two Systems in Thermal Contact

- Bridging over to thermodynamics
- Bridging over to canonical ensemble

> Key concepts here!

To bring out the idea, consider two tiny† systems

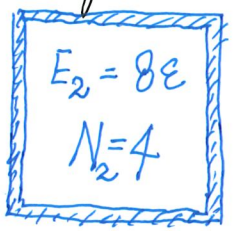
Physical Sense "Colder" $\left(\frac{E}{N} = 1\right)$ → System [1]



$W^{(1)} = \frac{7!}{4!\,3!} = 35$

↑ # microstates

Physical Sense "Hotter" $\left(\frac{E}{N} = 2\right)$ → System [2]



$W^{(2)} = \frac{11!}{8!\,3!} = 165$

What happens if bring systems into thermal contact?

↳ [can exchange energy]

(not exchanging particles)

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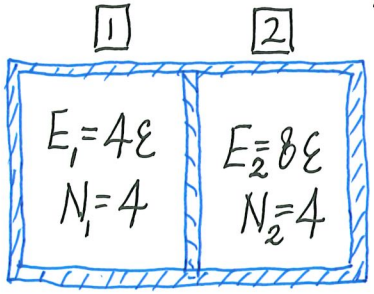
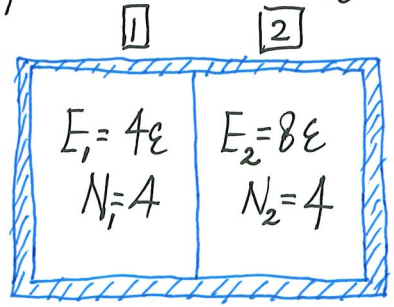
† Real systems are usually with numbers that are $(10^{24}!)$ bigger (10^{24} factorial bigger).

What will happen if we put them into thermal contact?

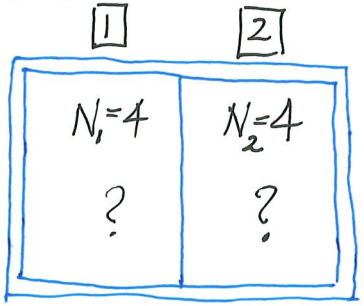


Not in thermal contact



↳ The moment [1] & [2] are put into thermal contact

as time goes by → ??



"equilibrium"

Thermodynamics:

The composite system is out of equilibrium [colder | hotter]

→ spontaneous process (entropy increases)

Equilibrium (same temperature throughout)

How to analyze the physics from Stat. Mech. viewpoint?

Initial Situation (take left-most figure : it is an equilibrium state)

[1] $W^{(1)} = 35$, [2] $W^{(2)} = 165$ $\therefore W^{initial} = 35 \times 165 = 5775$

microstates before thermal contact

With Thermal Contact

- Wall allows exchange of energy [wall doesn't move, wall has NO Pores]
- E = Total energy available to Composite System = 12ε

The total energy 12ε (E) can be shared by [1] and [2] in all possible ways, i.e. (E_1, E_2) can be (0,12), (1,11), (2,10), (3,9), (4,8), (5,7), (6,6), (7,5), (8,4), (9,3), (10,2), (11,1), (12,0).

↑ This is initial situation

[(0,12) means zero energy in [1] and $E = 12\varepsilon$ all in [2]]

For each allocation of E to [1] and [2], there is a corresponding number of microstates.

Example: $(E_1 = 2,\ E_2 = 10)$ $[N_1 = 4,\ N_2 = 4]$

$$W_1(E_1 = 2) = \frac{5!}{2!\,3!} = \underbrace{10}_{\text{see table}}, \quad W_2(E_2 = E - E_1 = 10) = \frac{13!}{10!\,3!} = \underbrace{286}_{\text{see table}}$$

$\therefore$ # microstates for this $(E_1 = 2, E_2 = 10)$ allocation of E

$$= W_1(E_1 = 2) \cdot W_2(E_2 = E - E_1 = 10) = 2860$$

We can work out the numbers for all (E_1, E_2) allocations to [1] & [2].

$E = 12\varepsilon$ $\quad N_1 = 4,\ N_2 = 4$

(E_1, E_2)	(0,12)	(1,11)	(2,10)	(3,9)	(4,8)	(5,7)	(6,6)	(7,5)	(8,4)	(9,3)	(10,2)	(11,1)	(12,0)
$W_1(E_1)$	1	4	10	20	35	56	84	120	165	220	286	364	455
$W_2(E_2)$	455	364	286	220	165	120	84	56	35	20	10	4	1
$W_1(E_1) \times W_2(E_2)$	455	1456	2860	4400	5775	6720	**7056**	6720	5775	4400	2860	1456	455

(50388) ← total

Points to note and Concepts

- After composite system achieves equilibrium, ALL accessible Microstates are equally probable

$$\#\ \text{Microstates after [1] \& [2] in equilibrium} = \sum_{E_1=0}^{E} W_1(E_1) \cdot W_2(E_2) = \sum_{E_1=0}^{E} W_1(E_1) \cdot W_2(E - E_1) \quad \text{(General)} \quad (21)$$

In our case, add up all $W_1(E_1) \cdot W_2(E_2)$ [add 13 numbers]

$$W_{total}(E, N_1, N_2) = 50388$$ (after allowing thermal contact and wait)

$W_{initial} = 5775$; $W_{final} = 50388$

$S_{initial} = k \ln W_{initial}$; $S_{final} = k \ln W_{final} > S_{initial}$

irreversible process occurs when one side is hotter than the other

- $W_{total} = 50388$

there is a particular allocation of E that carries the largest number of microstates[+]

In our example, ($E_1 = 6\mathcal{E}$, $E_2 = 6\mathcal{E}$) carries 7056 microstates out of W_{total} (50388)

The dominance of one particular allocation will be overwhelming in $N \sim 10^{23}$ systems (22)

[+] This can be thought of as the most Probable Distribution of energy between the two subsystems in thermal contact.

Physical sense

From $\left(E_1^{\text{initial}} = 4\varepsilon,\ E_2^{\text{initial}} = 8\varepsilon\right)$ to the dominating final allocation $(E_1 = 6\varepsilon,\ E_2 = 6\varepsilon)$

- 2 units of energy go from the higher $\left(\frac{E_2^{\text{initial}}}{N_2}\right)$ side (hotter side [2])
  to the lower $\left(\frac{E_1^{\text{initial}}}{N_1}\right)$ side (colder side [1])
- thermodynamic thinking: Q leaves [2] $\Rightarrow$ drop in entropy $\sim \frac{-Q}{T_{[2]}}$
  Q enters [1] $\Rightarrow$ increase in entropy $\sim \frac{+Q}{T_{[1]}}$

$$T_{[1]} < T_{[2]} \Rightarrow \Delta S > 0$$

[Statistical Mechanics considerations are consistent with thermodynamics]

- $E_1 = 6\varepsilon \Rightarrow \frac{E_1}{N_1} = \frac{6}{4}$ $\qquad$ $E_2 = 6\varepsilon \Rightarrow \frac{E_2}{N_2} = \frac{6}{4}$

↖ "same temperature" ↗

(E_1,E_2)	(0,12)	(1,11)	(2,10)	(3,9)	(4,8)	(5,7)	(6,6)	(7,5)	(8,4)	(9,3)	(10,2)	(11,1)	(12,0)
$W_1(E_1)$	1	4	10	20	35	56	84	120	165	220	286	364	455
$W_2(E_2)$	455	364	286	220	165	120	84	56	35	20	10	4	1
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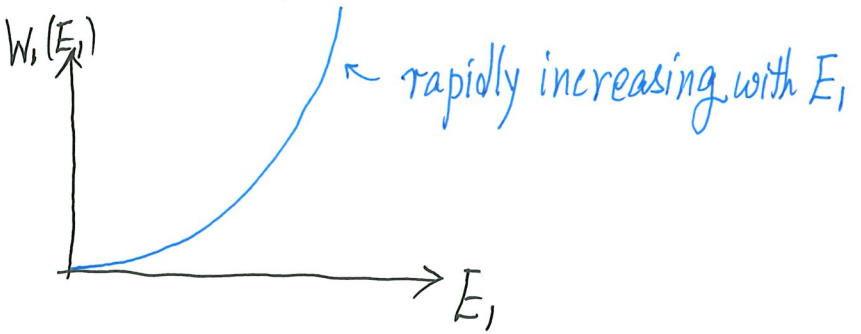
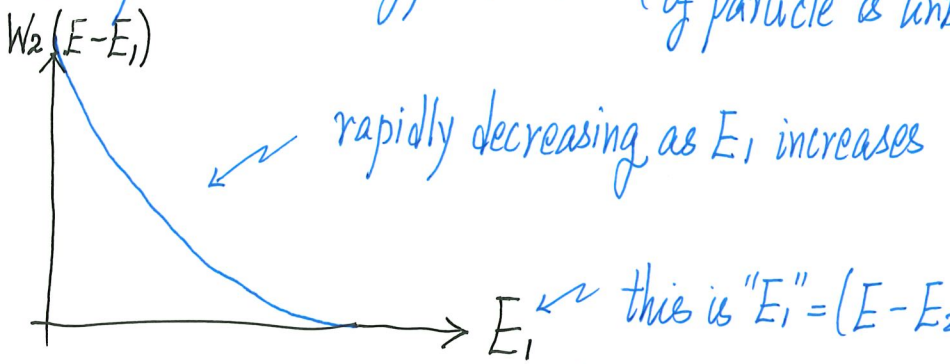
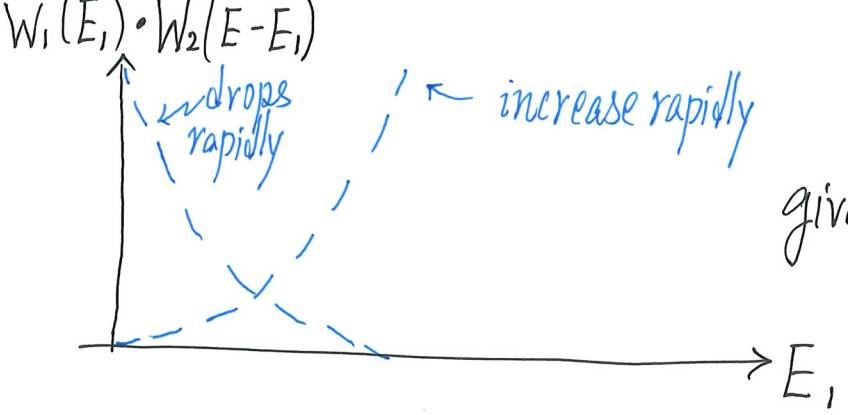
More detailed analysis

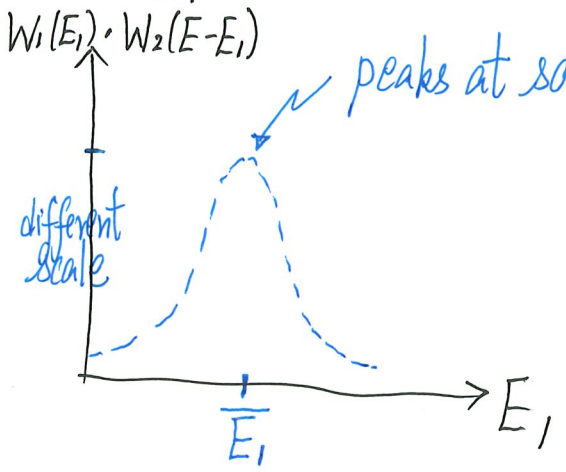
See $W_1(E_1)$ ← how # microstates in [I] depends on energy E_1 in [II] (Note: energy spectrum of particle is unbounded)



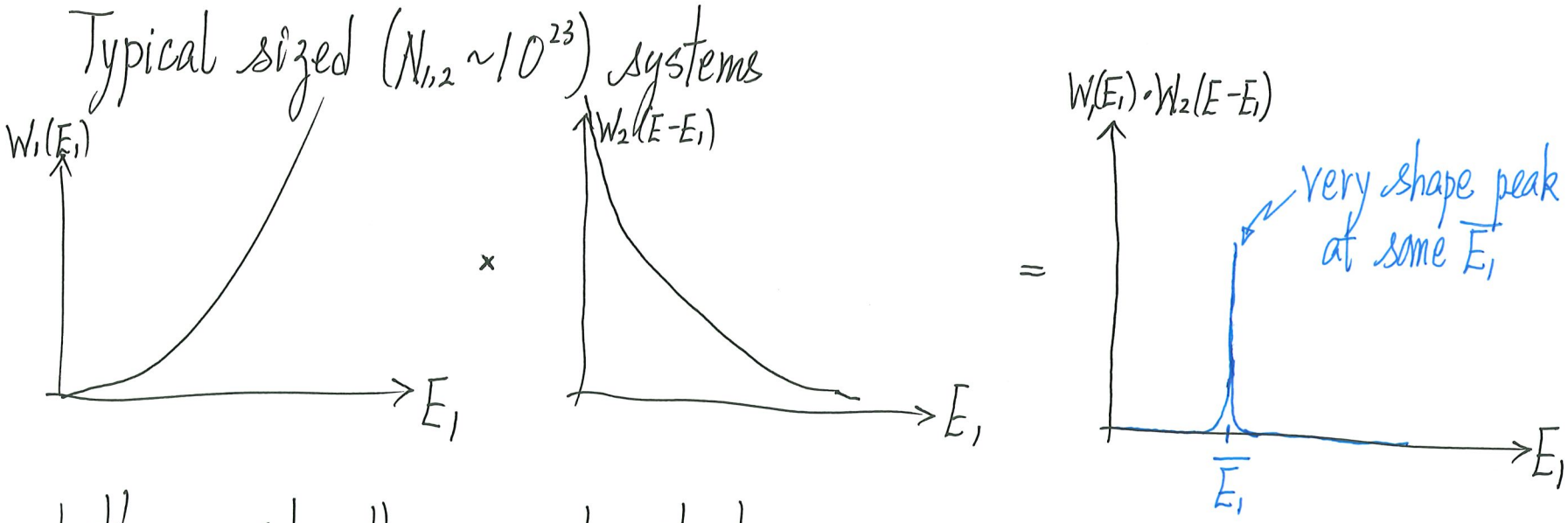




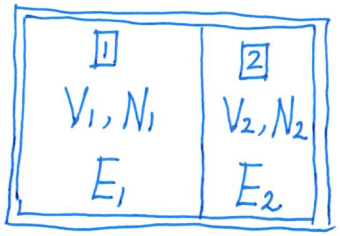
gives



Typical sized ($N_{1,2} \sim 10^{23}$) systems



- Let's consider the general situation



with $E = E_1 + E_2$ (E fixed)

- An allocation of E to 1 & 2: (E_1, V_1, N_1) and (E_2, V_2, N_2)

$$\#\text{microstates} = W_1(E_1, V_1, N_1) \cdot W_2(E_2, V_2, N_2) \qquad (E_1 + E_2 = E)$$

$$W_{total}(E, \underbrace{N_1, N_2}_{N=N_1+N_2,\ N \text{ fixed}}, \underbrace{V_1, V_2}_{V=V_1+V_2,\ V \text{ fixed}}) = \sum_{E_1=0}^{E} W_1(E_1, V_1, N_1) \cdot W_2(E-E_1, V_2, N_2) = \text{a huge number} \qquad (21)$$

All W_{total} microstates are equally probable

but one term in W_{total} dominates (key concept here!)

$$W_1(\bar{E}_1, V_1, N_1) \cdot W_2(E-\bar{E}_1, V_2, N_2) \text{ out numbers all other terms}$$

- What is so special about this particular $(\bar{E}_1, E_2 = E-\bar{E}_1)$ partition of energy?

$W_1(E_1, V_1, N_1) \cdot W_2(E-E_1, V_2, N_2)$ has a sharp maximum at $E_1 = \bar{E}_1$

$\therefore$ $\ln[W_1(E_1, V_1, N_1) \cdot W_2(E-E_1, V_2, N_2)]$ has a maximum† at $E_1 = \bar{E}_1$ (23)

[$\ln x$ is a monotonic function of x]

$x \uparrow \quad \ln x \uparrow$

$x \downarrow \quad \ln x \downarrow$

† $\ln[\text{something}]$ is a much slowly varying function than [something]. This makes derivatives easier to take.

Mathematically, (23) means $\frac{\partial}{\partial E_1} \ln\left[W_1(E_1, V_1, N_1) \cdot W_2(\overbrace{E-E_1}^{E_2}, V_2, N_2)\right]\Big|_{E_1=\bar{E}_1} = 0$ (24)

$$\Rightarrow \left.\frac{\partial \ln W_1(E_1,V_1,N_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} + \left(\frac{\partial}{\partial E_2}\ln W_2(E_2,V_2,N_2)\cdot \underbrace{\frac{\partial E_2}{\partial E_1}}_{\text{"}-1\text{"}}\right)\Bigg|_{E_1=\bar{E}_1} = 0$$

$$\Rightarrow \boxed{\left.\frac{\partial \ln W_1(E_1,V_1,N_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} = \left.\frac{\partial \ln W_2(E_2,V_2,N_2)}{\partial E_2}\right|_{E_2=\bar{E}_2=E-\bar{E}_1}} \quad (25)$$

What is so special at $E_1 = \bar{E}_1$?

Microscopically speaking: Two systems have common $\left(\frac{\partial \ln W}{\partial E}\right)$

Thermodynamics: Two systems have a common temperature $T_{[1]} = T_{[2]}$

Consistent! $\frac{1}{T} = \left(\frac{\partial k \ln W}{\partial E}\right)_{N,V}$

∴ We re-discovered Zeroth Law from Stat. Mech.

Remarks

- Macroscopically (thermodynamics) speaking, we always (almost always) observe the partition of energy $\bar{E}_1 = U_1$ in [1] and $\bar{E}_2 = U_2$ in [2], and that the two systems shared a common temperature when they are in equilibrium with each other.

- Statistical Mechanics viewpoint

  (a) two systems at equilibrium has a dominating partition of energy $\bar{E}_1$ and $\bar{E}_2 = E - \bar{E}_1$, the special point about this partition is that $\left(\frac{\partial\, k \ln W}{\partial E}\right)$ at the same for the systems

Formally, one can DEFINE the temperature (in stat. mech) at this point by

$$\frac{1}{T} = \frac{\partial k \ln W(E,V,N)}{\partial E}$$

without knowing any thermodynamics

Then, stat. mech. discovered that $T_1(\bar{E}_1, V_1, N_1) = T_2(\bar{E}_2, V_2, N_2)$
for two systems in equilibrium through exchange of energy

$\Rightarrow$ Zeroth Law of Thermodynamics Without knowing thermodynamics

Using $S = k \ln W(E, V, N)$, also discovered the term

$$dE = TdS \qquad (V, N \text{ constant})$$

which is one term in Central Equation Without knowing thermodynamics.

This is the approach in some statistical mechanics books

[NOT my approach in this course]

(b) Bridging Over to Canonical Ensemble Approach (Key concepts here)

When we have two systems in equilibrium and two systems can (only) exchange energy, all W_{total} microstates are equally probable.

Probability of finding System [1] having energy E_1

$$= \frac{W_1(E_1, V_1, N_1) \cdot W_2(E - E_1, V_2, N_2)}{W_{total}} \qquad (26)$$

Key equation for deriving the Boltzmann Distribution and Partition Function

the most important result in "Canonical Ensemble"

We will pick up the discussion from Eq. (26) in next Chapter

K. Temperature and S at T=0

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

"low temp." means adding in a bit of energy and # microstates increases rapidly

"high temp." means adding in a bit of energy and # microstates only increases a bit

Ground State [Lowest Possible energy of a N-particle system]

e.g. N 2-level particles — up / — low

Ground state is: {low, low, low, ..., low, ...} [1 string]

⇒ 1 microstate

[Unique Ground State]

$$S = k \ln 1 = 0$$

T=0, system is in Ground State

∴ S(T=0) = 0 (consistent with 3rd law)

Summary

- Isolated system (E, V, N) at equilibrium, all microstates are equally probable
- $S(E, V, N) = k \ln W(E, V, N)$

If you understand the validity (conditions) and how to apply this calculation scheme, you know ALL the Principles of Equilibrium Statistical Mechanics.

All other topics are consequences or by-products! (no new principles!)

With solid understanding of Ch. VIII and key thermodynamics relations, you should be able to learn other topics in Stat. Mech. by yourself.