High Entropy Alloys

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Alloys

What are they?

Mixture of multiple elements
At least one is a metal

Why?

Produce useful properties
Offset undesirable ones

Cu + Sn → Bronze

Fe + Cr → Stainless Steel

Rusts!

Cu + Zn → Brass

Pb + Sn → Solder

Synthesis

Choose a base metal (Iron)

Melt. This will be the solvent

Add the solute metals (Chromium)

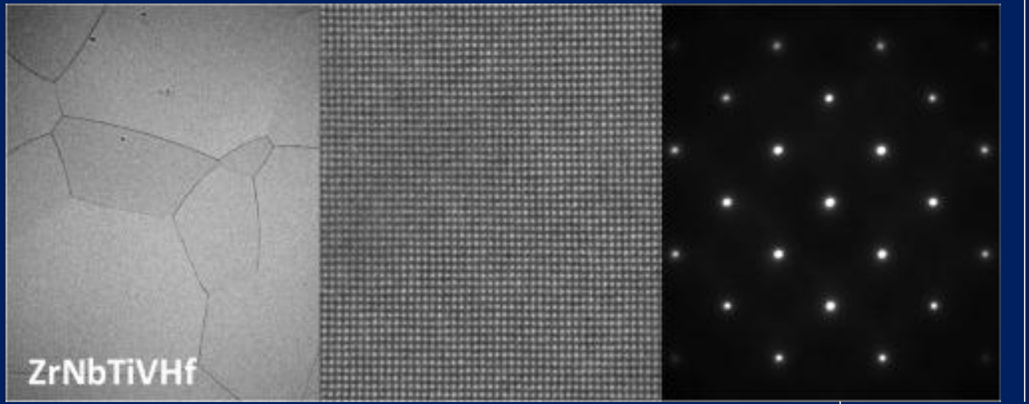
Cast into chosen shape and cool

Solute must mix!

Solidification

Single-phase (Solid Solution)

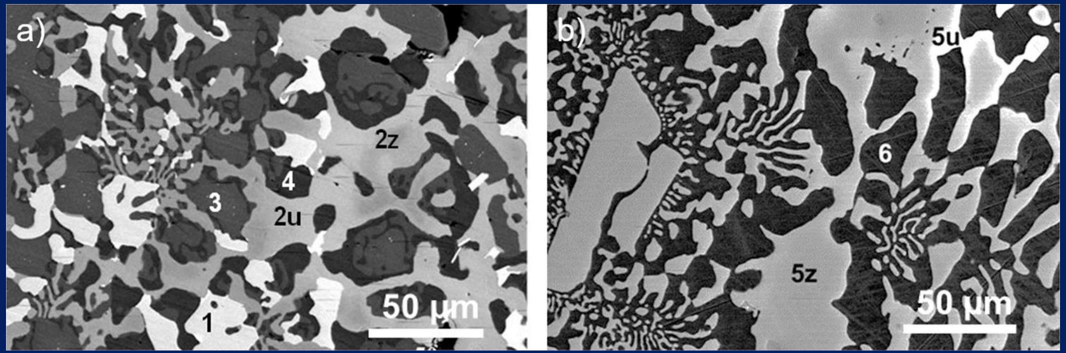
Homogenous
This means there is the same composition of elements everywhere



Periodic!

Multi-phase (Intermetallics)

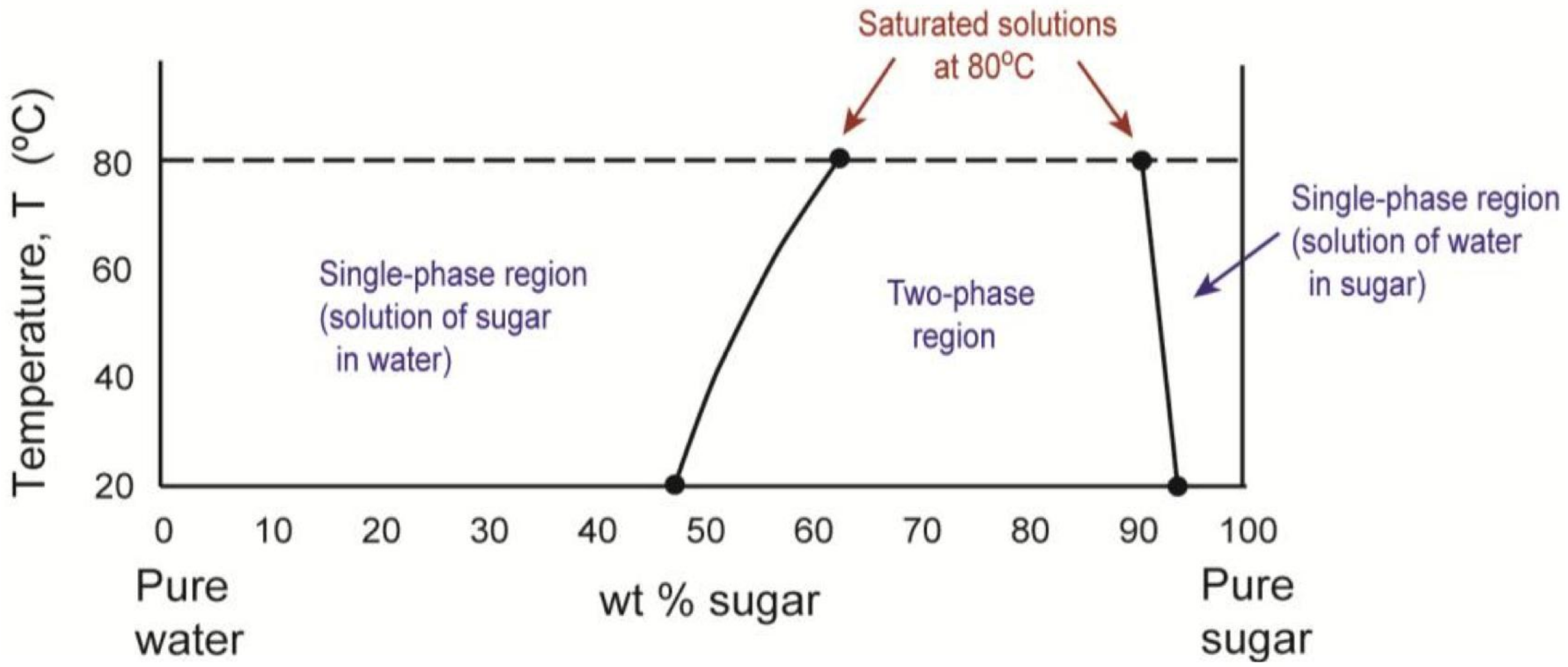
Heterogenous
This means that there are compounds with different compositions present in the alloy



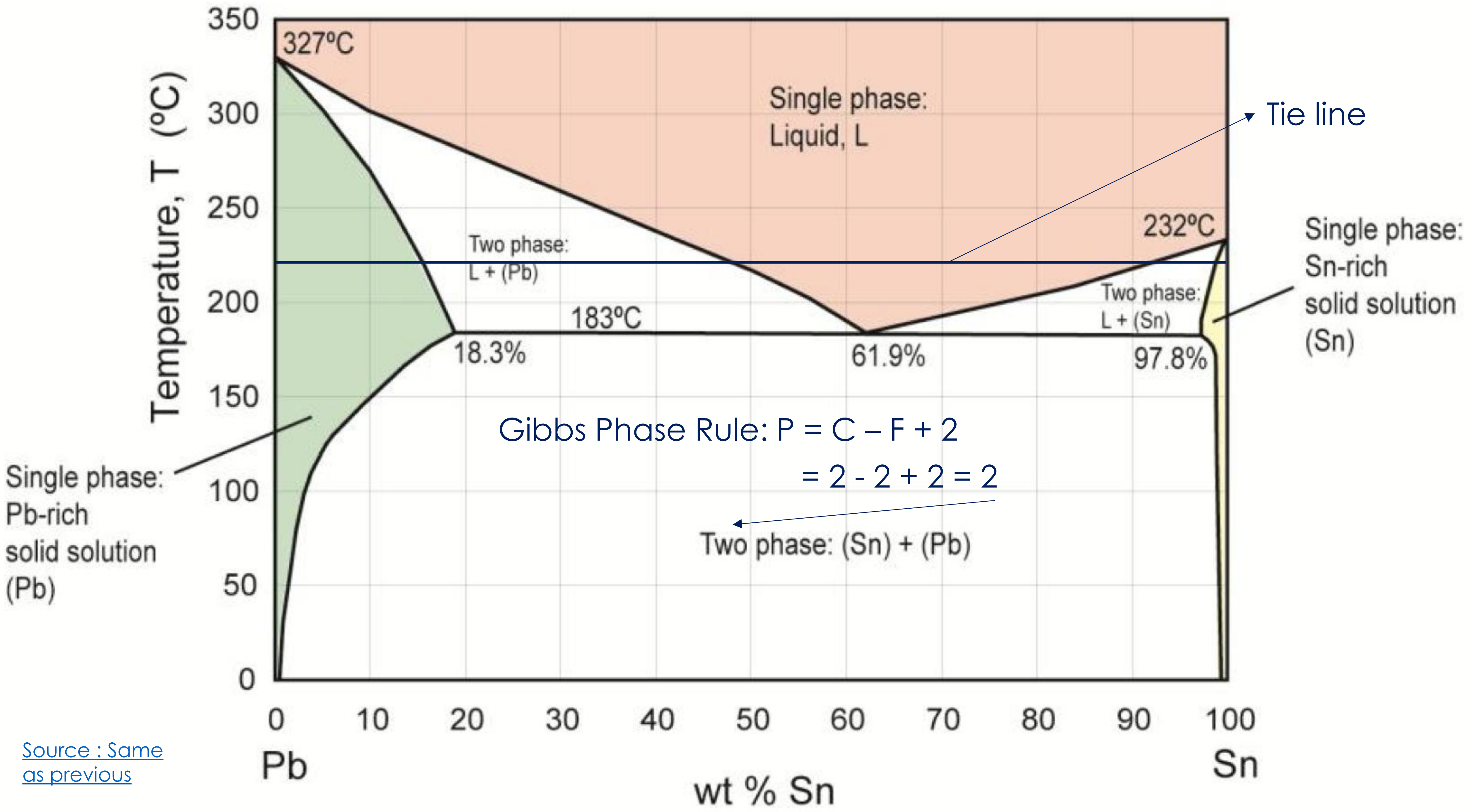
M. Feuerbacher, T. Lienig, C. Thomas, Scripta Materialia, 152, 40 (2018)
V.K. Gattu, W. L. Ebert, J.E. Indacochea *et al*, npj Mater Degrad 6, 14 (2022)

Phase Diagram

It is one of the most important diagrams for material scientists and engineers!
It shows all the different phases at different solute-solvent percentages.



https://www.grantadesign.com/download/pdf/edupack2015/Teach_Yourself_Phase_Diagrams_and_Phase_Transformations.pdf



[Source : Same as previous]()

Video Evidence

Melt on Mix

https://www.youtube.com/watch?v=6_EHAaMEc2A

Current alloying scheme

Base Metal + Additional Elements

This is also called the principal element
It has the highest concentration in the alloy
What happens if we have many elements?

Gibbs Phase rule says…

More elements, More phases

Could it be possible to get single-phase system with many base components?

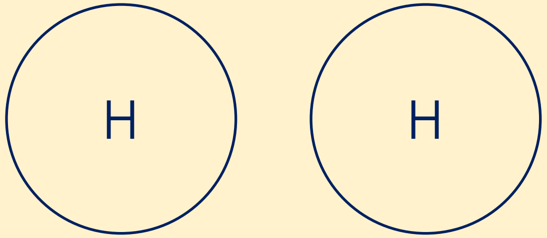
Prof. Brian Cantor

Prof. Jien-Weh Yeh

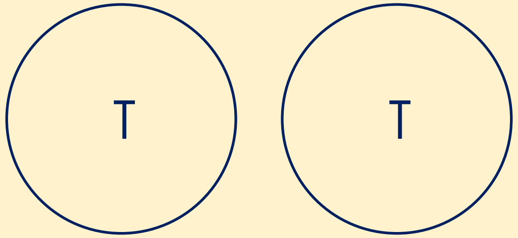
Entropy

Definition: $S = k\log(N)$, where N refers to number of arrangements. **But what does it mean?**

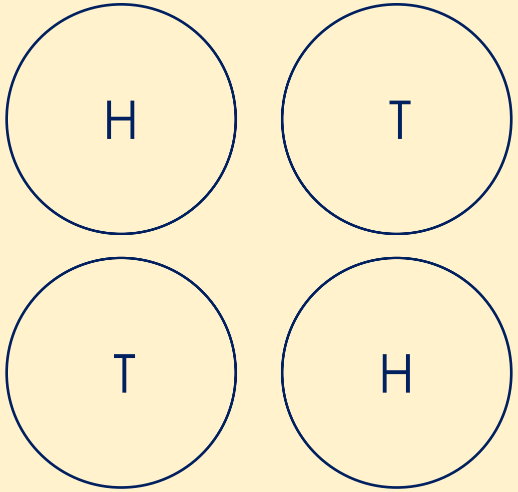
2 unbiased coins



Only one arrangement
$S = k\log(1) = 0$

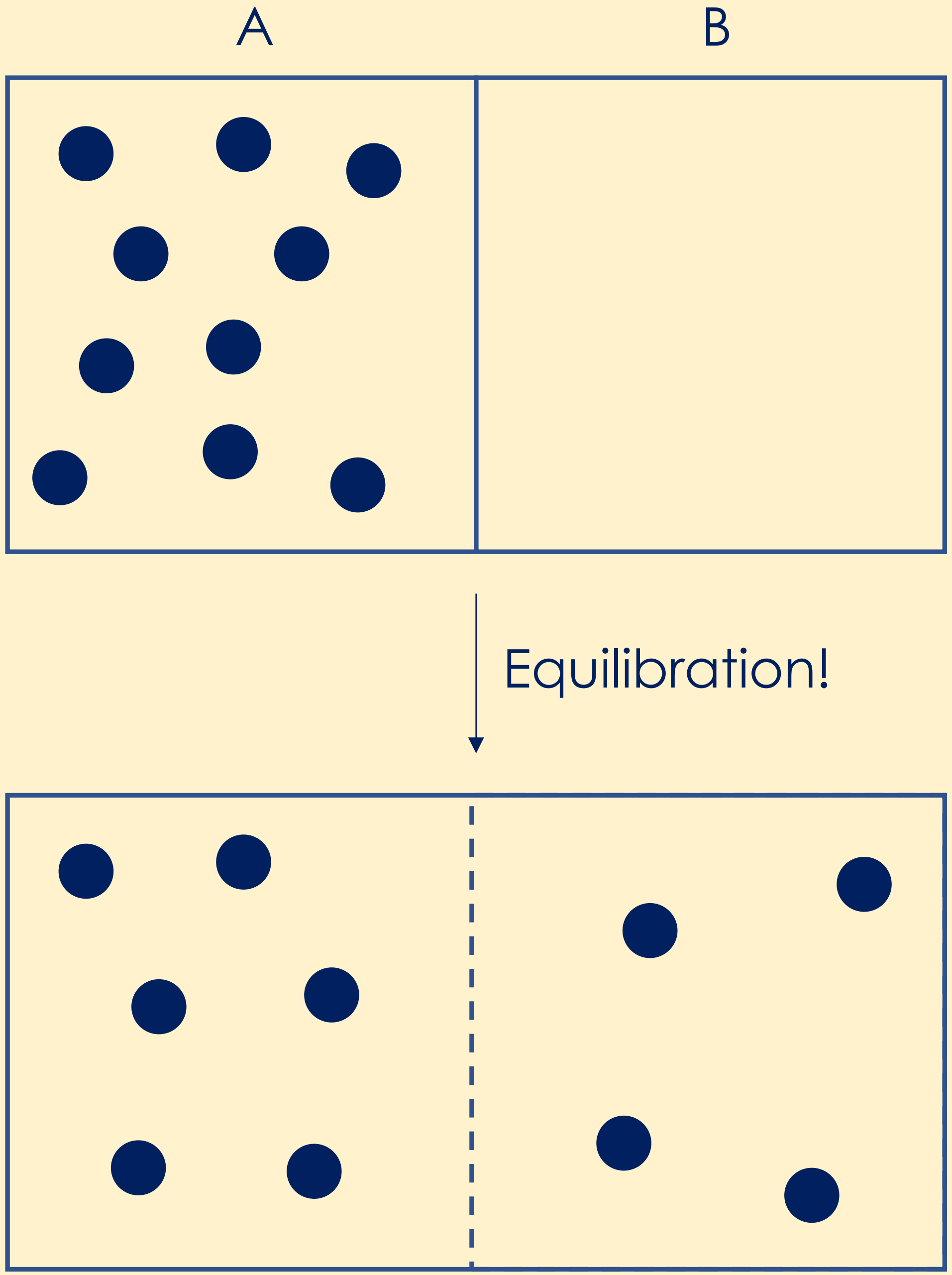


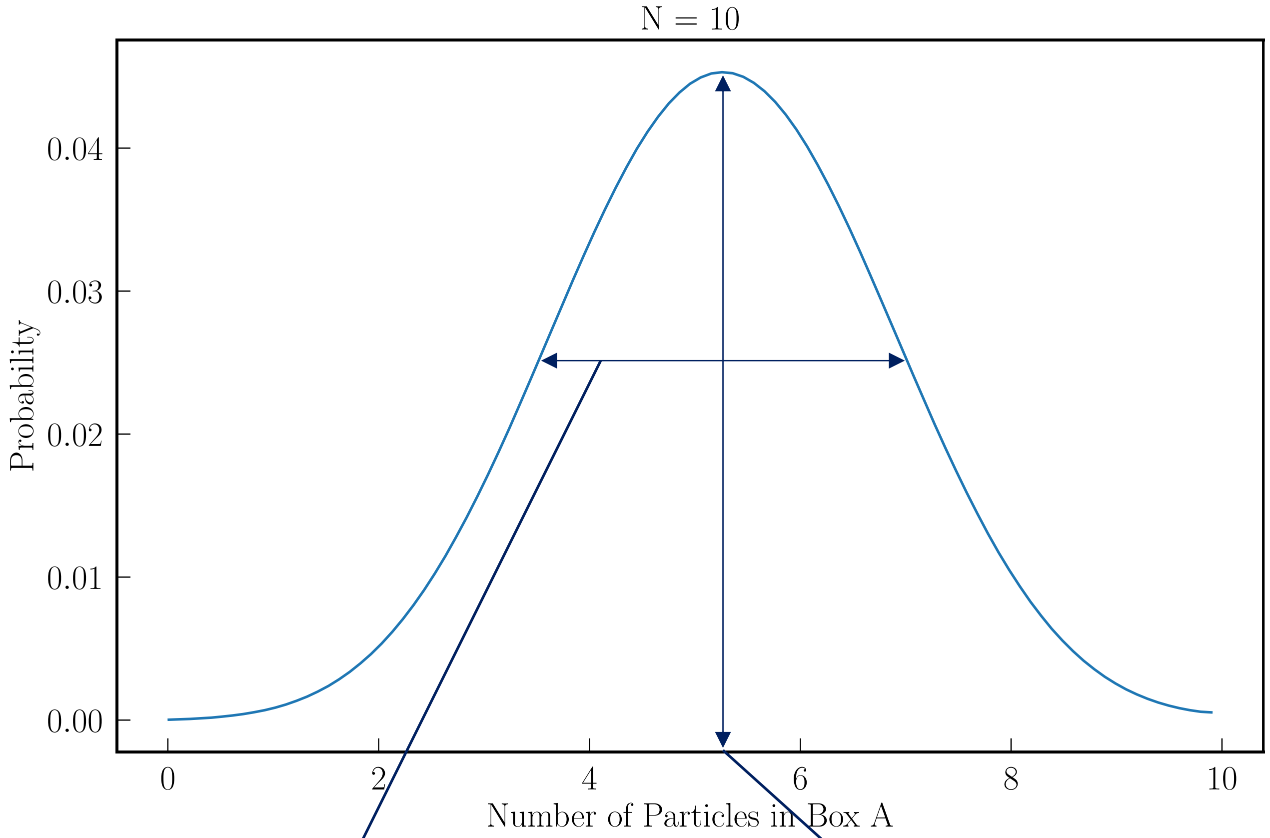
Only one arrangement
$S = k\log(1) = 0$



Two arrangements
$S = k\log(2)$

More arrangements, higher entropy!

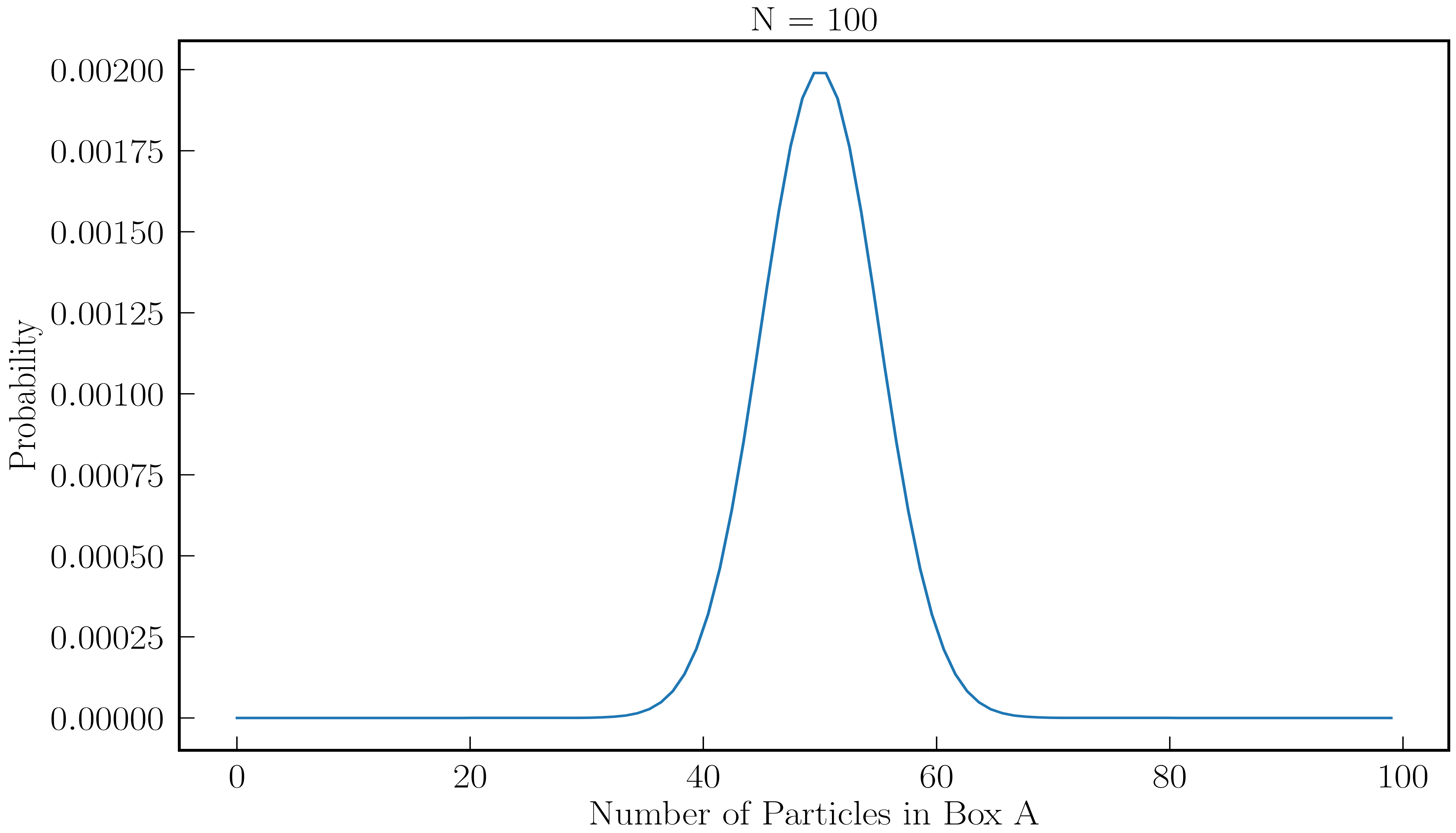


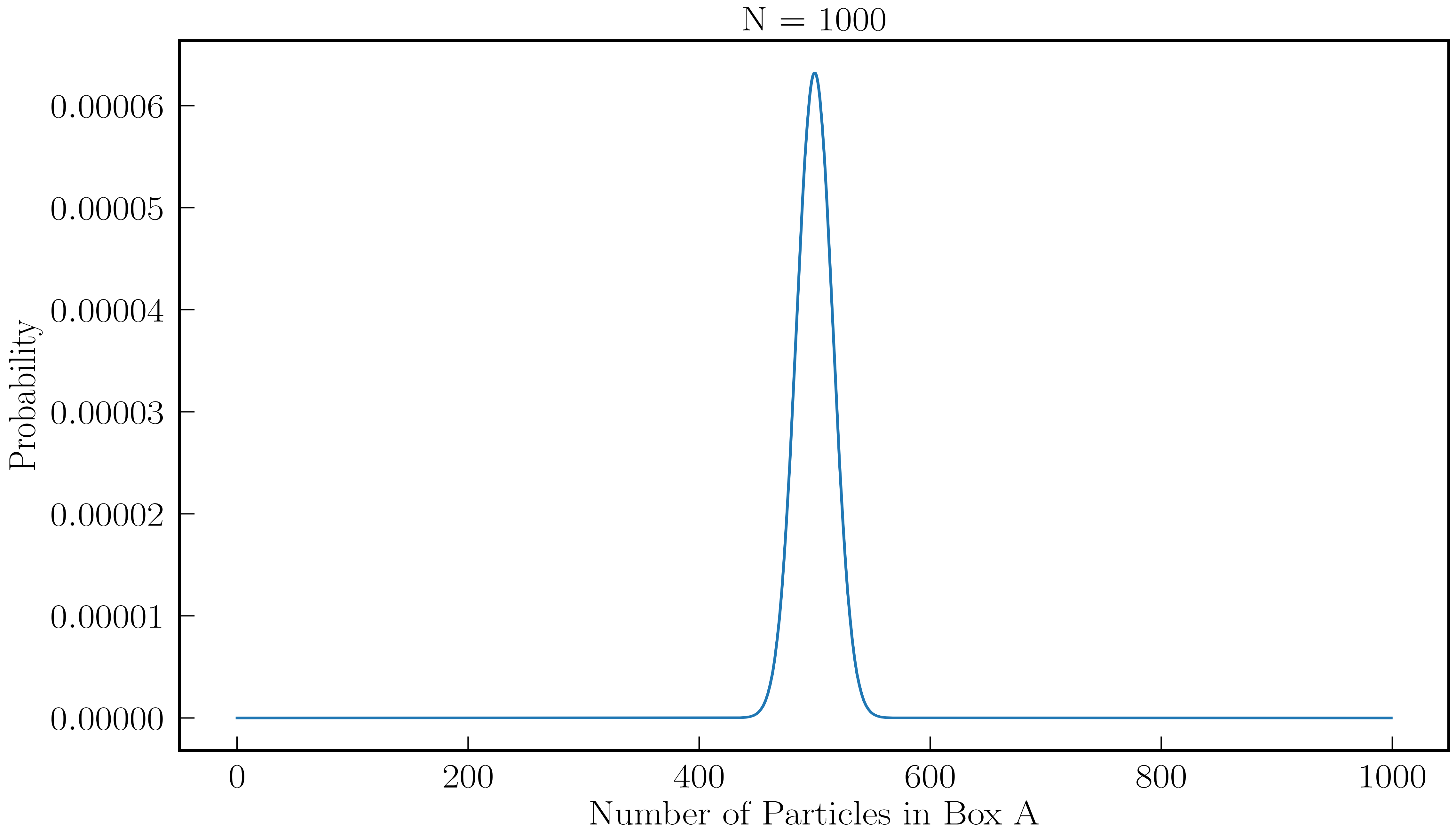


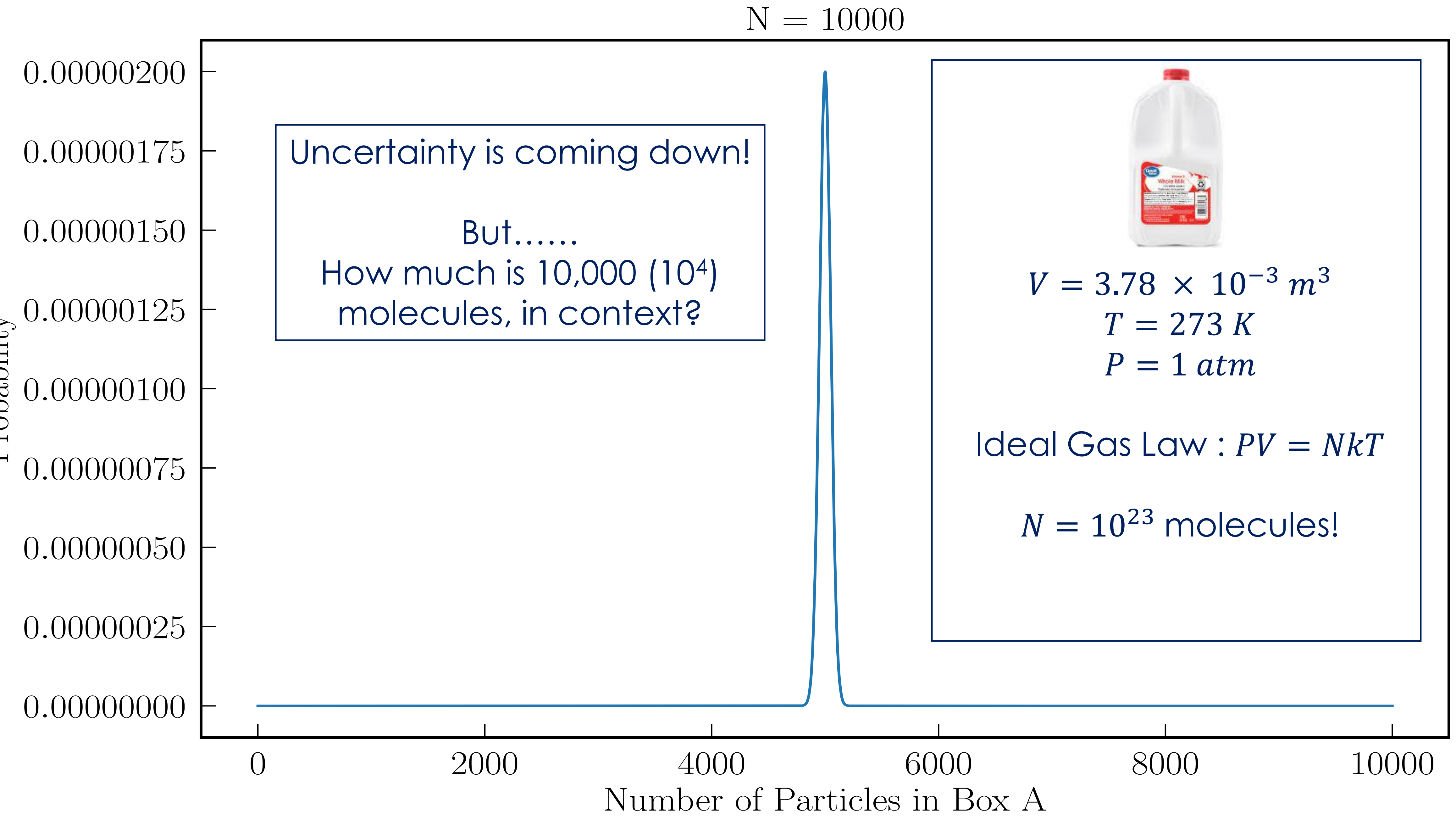
Uncertainty!

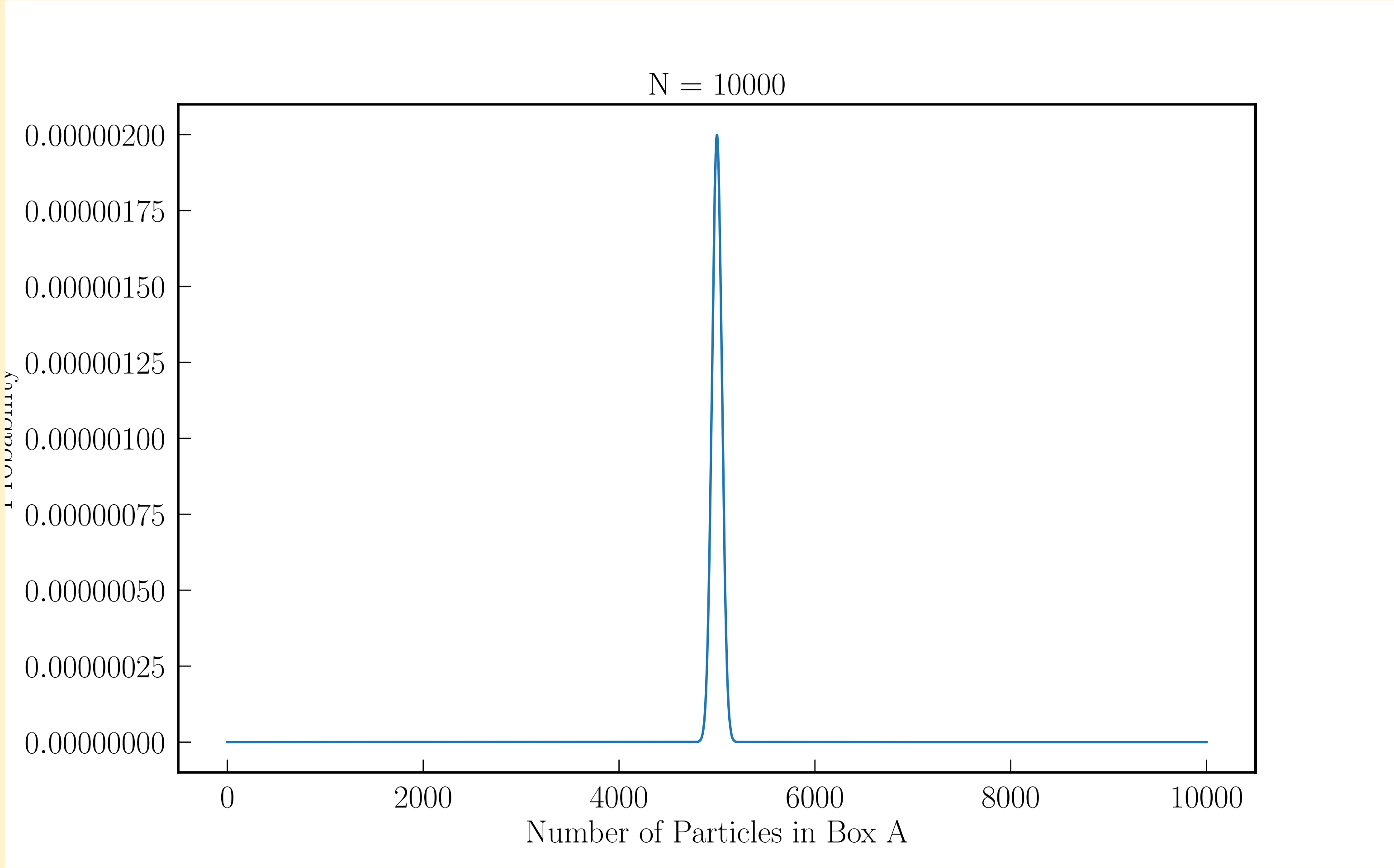
What happens at larger N?

Most likely value. (Nearly!) Corresponds to maximum entropy


N = 100
0.00200
0.00175
0.00150
0.00125
0.00100
0.00075
0.00050
0.00025
0.00000
Probability
0
20
40
60
80
100
Number of Particles in Box A


N = 1000
Probability
0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
0.00000
0
200
400
600
800
1000
Number of Particles in Box A

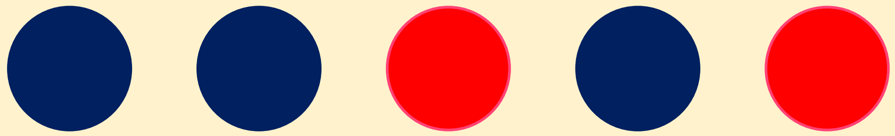

N = 10000
0.00000200
0.00000175
0.00000150
0.00000125
0.00000100
0.00000075
0.00000050
0.00000025
0.00000000
0
2000
4000
6000
8000
10000
Number of Particles in Box A
Uncertainty is coming down!
But……
How much is 10,000 (10^4)
molecules, in context?
Whole Milk
$V = 3.78 \times 10^{-3}\ m^3$
$T = 273\ K$
$P = 1\ atm$
Ideal Gas Law : $PV = NkT$
$N = 10^{23}$ molecules!



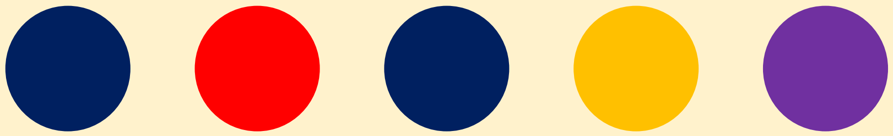
When $N \rightarrow \infty$, there is no uncertainty. The system will go to maximum probability state.
When left alone, the system tries to maximize its entropy.

This is called the **second law of thermodynamics.** *It's a fundamental law of nature*

What does this have to do with alloys?



$$N = \frac{5!}{3!\,2!} = 10$$



$$N = \frac{5!}{2!} = 60$$

Could it be possible to get single-phase system with many base components?

Yes.

More elements, more entropy.

Nature favors higher entropy!

Free Energy and Single Phase

Nature wants to maximize entropy. It also wants to minimize energy.
How to incorporate both? **Free Energy**

$$\Delta F = \Delta E - T\Delta S$$

If both temperature and entropy are high enough, this term will dominate

$\boldsymbol{\Delta F < 0}$

This process will happen naturally

$\boldsymbol{\Delta F > 0}$

This process must be forced through

While this idea was around since the 90s, the field really kicked off with this **2004** paper by Yeh *et al*

Nanostructured High-Entropy Alloys with Multiple Principal Elements: Novel Alloy Design Concepts and Outcomes**

By *Jien-Wei Yeh,* Swe-Kai Chen, Su-Jien Lin, Jon-Yiew Gan, Tsung-Shune Chin, Tao-Tsung Shun, Chun-Huei Tsau,* and *Shou-Yi Chang*

8 components!

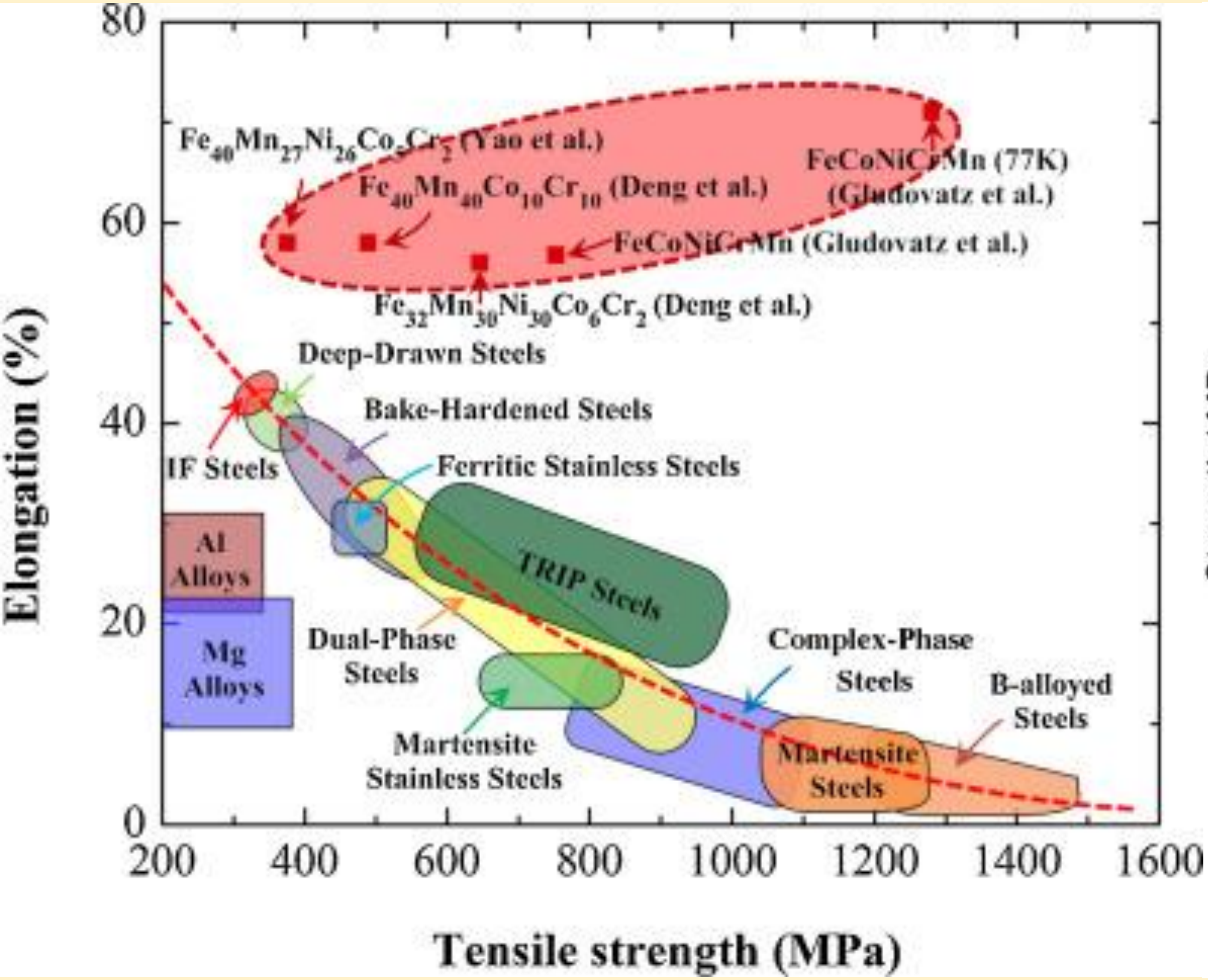
Table 1. Hardness of as-cast and fully annealed high-entropy alloys and commercial alloys. The high-entropy alloys exhibit very high hardness and excellent resistance to anneal softening even at 1000 °C for 12 h. Data scattering errors were within 3%.

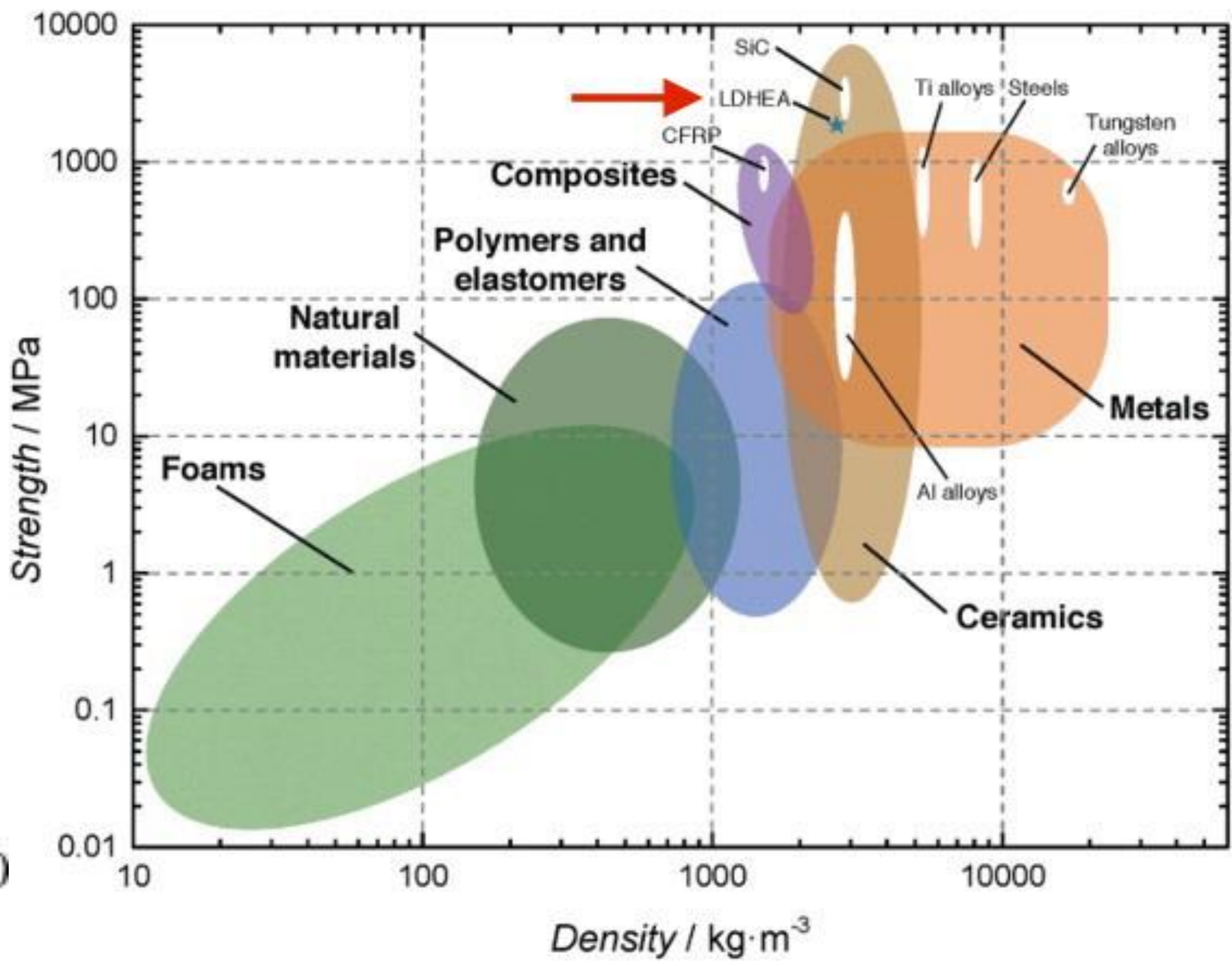
Alloys	Hardness, HV as-cast	Hardness, HV annealed
CuTiVFeNiZr	590	600
AlTiVFeNiZr	800	790
MoTiVFeNiZr	740	760
CuTiVFeNiZrCo	630	620
AlTiVFeNiZrCo	790	800
MoTiVFeNiZrCo	790	790
CuTiVFeNiZrCoCr	680	680
AlTiVFeNiZrCoCr	780	890
MoTiVFeNiZrCoCr	850	850
316 Stainless Steel	189	155
17-4 PH Stainless Steel	410	362
Hastelloy C[a]	236	280
Stellite 6[b]	413	494
Ti-6Al-4V	412	341

[a] Ni–21.5Cr–2.5Co–13.5Mo–4W–5.5Fe–1Mn–0.1Si–0.3V–0.01C in wt.-%, [b] Co–29Cr–4.5W–1.2C in wt.-%

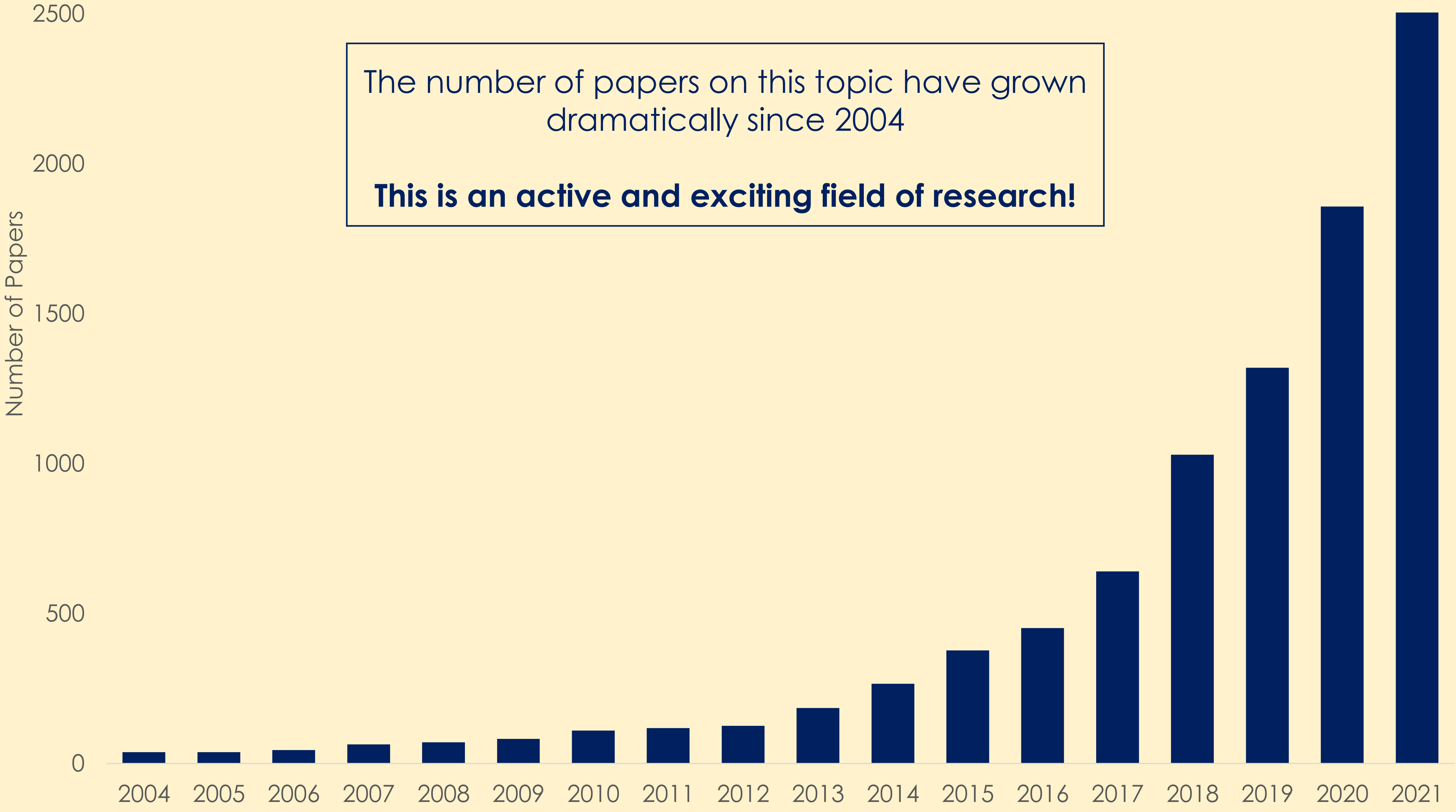
Higher strength and higher ductility!

$Al_{20}Li_{20}Mg_{10}Sc_{20}Ti_{30}$





Youssef *et al*, Materials Research Letters, 3:2, 95-99
Ye *et al*, Materials Today 19, 349 (2016)



The number of papers on this topic have grown dramatically since 2004
This is an active and exciting field of research!
Number of Papers
2500
2000
1500
1000
500
0
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021

What We Do

										5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
										13 Al Aluminium 26.982	14 Si Silicon 28.085	15 P Phosphorus 30.974	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948
21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
71 Lu Lutetium 174.97	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)

As can be seen, there are a LOT of elements they you can make high entropy alloys out of. However, only some of them will be useful, and we can't make all of them in a lab.

Solution? Simulate alloys on a computer

- Fast and (relatively) inexpensive
- Can create *any* type of structure, no practical concerns
- Can simulate *any* condition (e.g very low/high temperature or pressure)

How? Quantum Mechanics

The electrons in the system behave in accordance with the following equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi(r,t) + V(\boldsymbol{r})\psi(\boldsymbol{r},t) = i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t}$$

where ψ is called the "wavefunction". This equation can be solved on a computer. It is an intensive process and requires a **computing cluster**

Fugaku
RIKEN Center for Computational Science
Japan

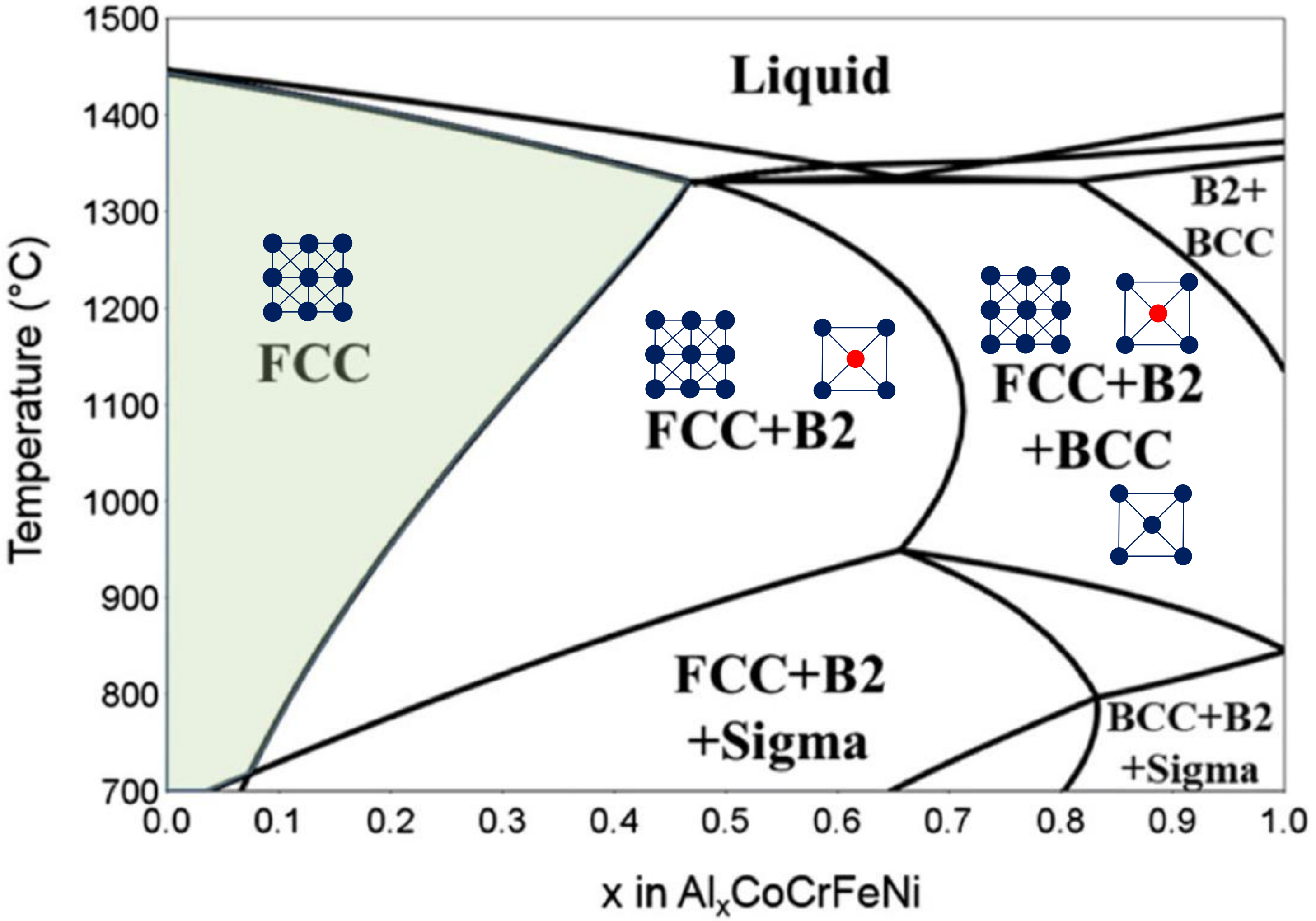
Bridges-2
Pittsburgh Supercomputing Center
USA

Euler
Widom Research Group, CMU
USA

Phase Diagrams

We can use a computational technique called **CALPHAD**, which stands for **CAL**culation of **PH**ase **D**iagrams

This analysis helps experimentalists to determine which concentrations and which temperature would be most suitable for a given purpose.

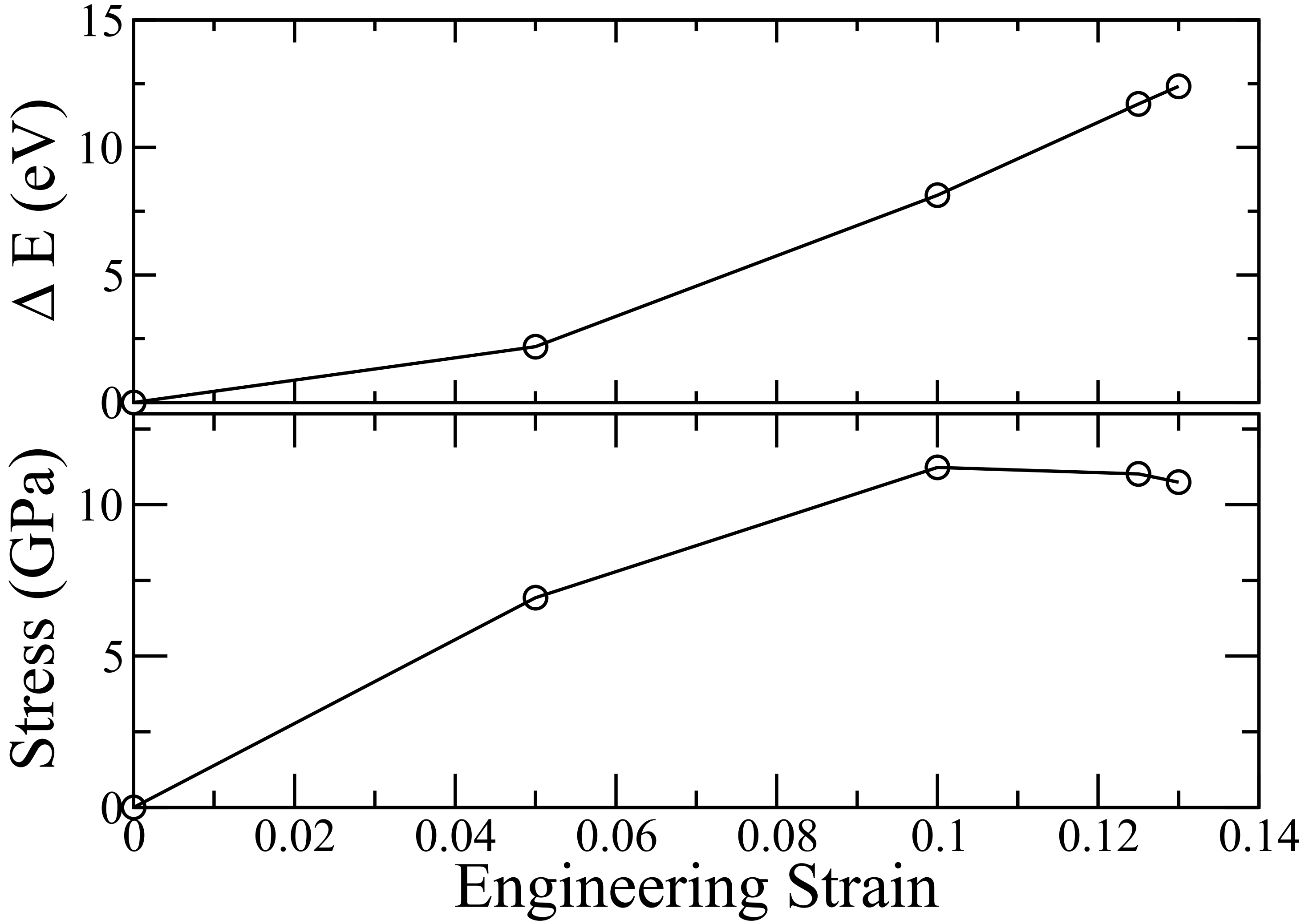


Ductility

We can computationally stretch the alloy (Hf-Nb-Ta-Ti-Mo) and calculate the mechanical energy and the induced stress as a function of the strain

If the stress **decreases** on stretching, the system has become unstable.

While there are more sophisticated methods to study ductility, this is a simple way to determine how "stretchable" an alloy is



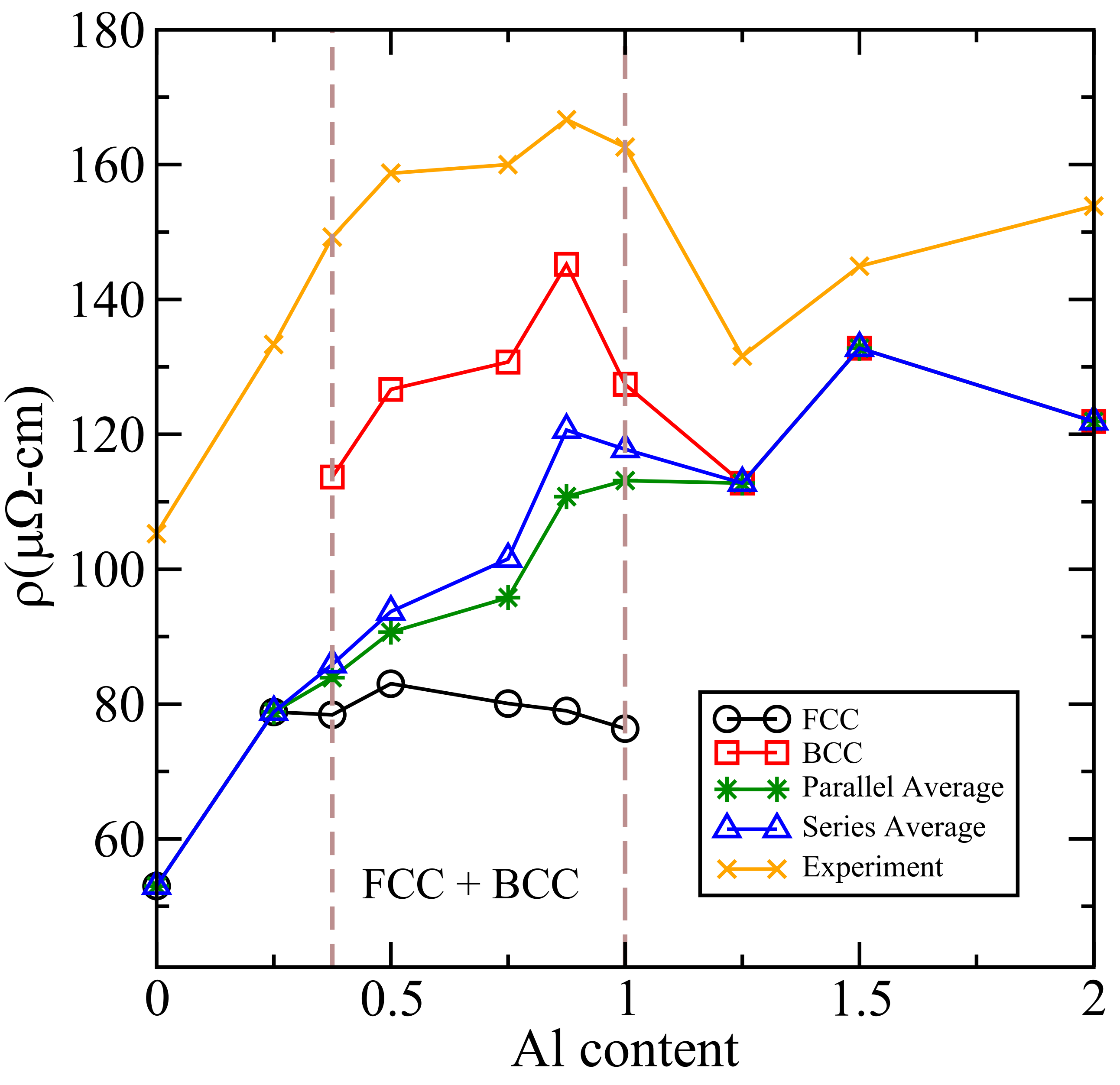
$Al_xCoCrFeNi$

Resistivity Study

This system has weird behavior in the intermediate (FCC+BCC) region.

The resistivity doesn't just keep going up, it dips a little due to changing structure of the alloy.

Our computational results (the red curve) manages to recreate the experimental trend.



Future

What's in store for this exciting field?

Easy and inexpensive manufacturing.

A better understanding of the physics.

Applications for clean energy production and storage

ARPA-E program ULTIMATE: Designing ductile turbine blades at high T

Thank you!
Any questions?