# MLL213: Materials Modelling

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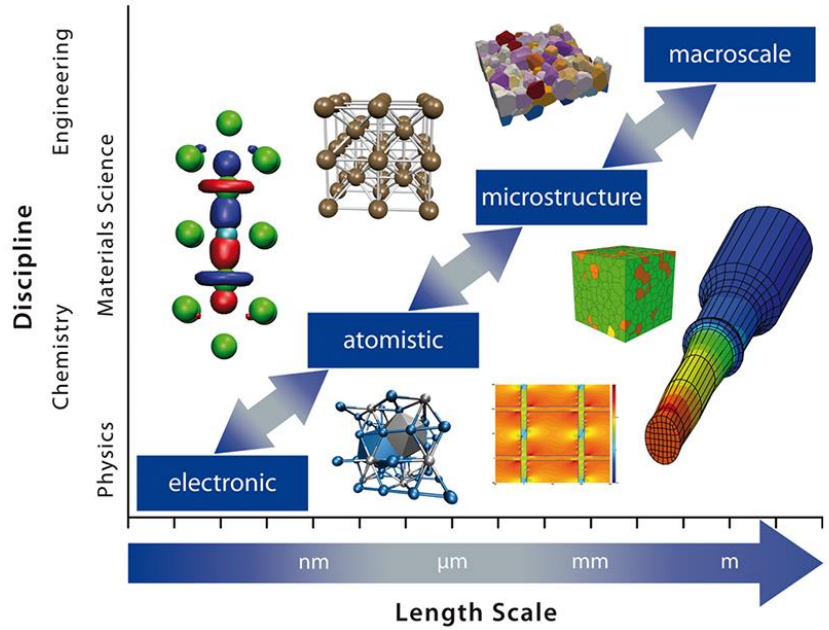


**Monte Carlo Methods**

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# Exercise 4: Energy of layer (change in CN)

a) Calculate the energy/atom of the unsupported (100) layer of SC-Al (PBC)

Calculate the energy/atom of the cluster of atoms in a 8 X 8 (100) layer of SC-Al shown below.

b) With Periodic Boundary Conditions

c) Without Periodic Conditions

d) Compare energies from a and b.
Comment on their magnitudes and give reasons.

**Use just first NN for energy calculation**

Use $R_o$ for SC-Al from exercise 2

X X X X X X X X
X X X X X X X X
O O X X X X O O
O O X X X X O O
O O X X X X O O
O O X X X X O O
X X X X X X X X
X X X X X X X X

O = Al atom
X = Vacancy

# Exercise 5: Energy of a layer

Let's continue with the layer from exercise 4. Assume that the system does not have PBC.

a) Write two functions, one to get the first NN CN and the other to get the second NN CN. Print the layer, its first NN Cn and second NN CNs.

b) Write a function to get the energy of a layer. Use first and second NN interactions for energy calculations

c) Calculate the energy of the layer by including the second nearest neighbors as well. Compare to energy from exercise 4c

d) Bonus: Can you find a better configuration that minimizes energy?

# Monte Carlo

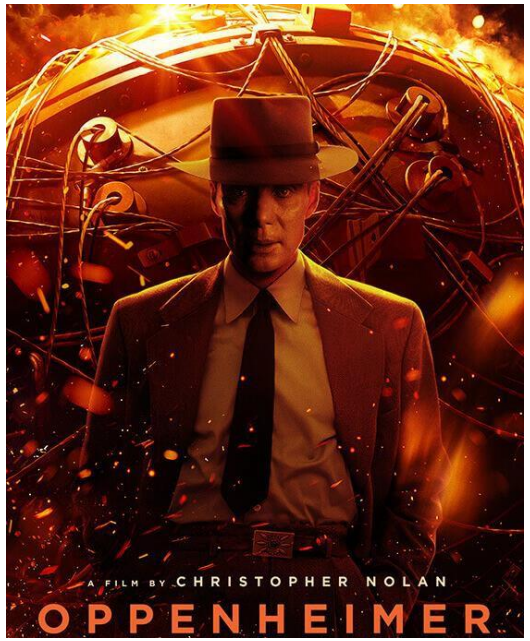

Casino de Monte-Carlo, Monaco

# Monte Carlo methods: Origins

- Monte Carlo methods were first developed during World War II as part of the **Manhattan Project**, the top-secret U.S. research and development effort to create the atomic bomb.

- Scientists and mathematicians working on the project, including **Stanislaw Ulam and John von Neumann**, faced complex mathematical and physical problems related to nuclear reactions and neutron diffusion.

- They realized that traditional numerical methods were inadequate for solving these problems, so they began **using random sampling** and statistical techniques to estimate results.




Neumann with Oppenheimer

# Monte Carlo methods : Origins

- The term "Monte Carlo" was coined by physicists Nicholas Metropolis, John von Neumann, and Stanislaw Ulam in 1947.
- They named it after the Monte Carlo Casino in Monaco, known for its games of chance, to emphasize the role of randomness in the method.
- In the post-war years, Monte Carlo methods found applications in a wide range of scientific and engineering disciplines, including aerospace engineering, statistical physics, and operations research.
- The technique gained popularity due to its versatility and ability to handle problems with complex geometry and high dimensionality.

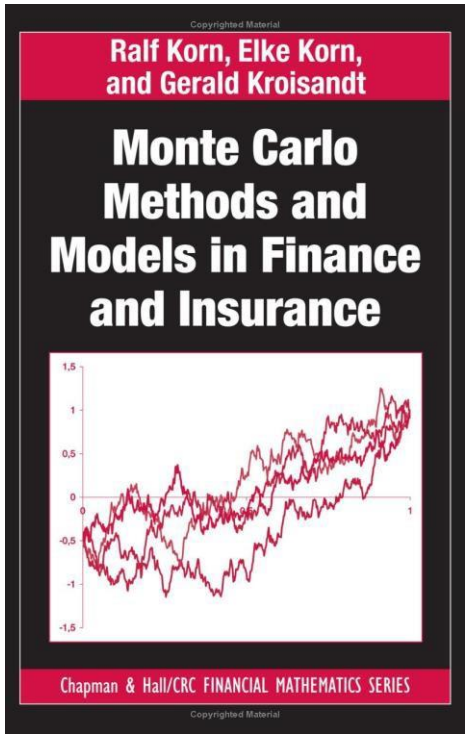
Paul Stein and Nicholas Metropolis
at the Los Alamos Scientific Laboratory

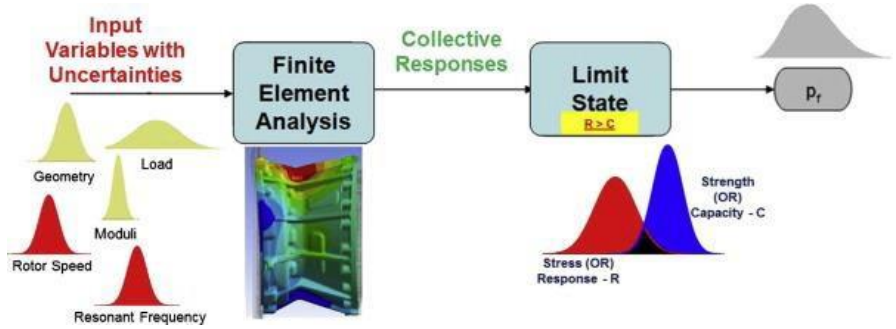
# Monte Carlo : Applications

- Availability of computers in the 1960s-70s significantly accelerated the development and widespread adoption of Monte Carlo methods.
- Statistics
- Computer science
- Finance
- Operational research
- Environmental science
- Chemistry
- Biomedical sciences
- Gaming and entertainment

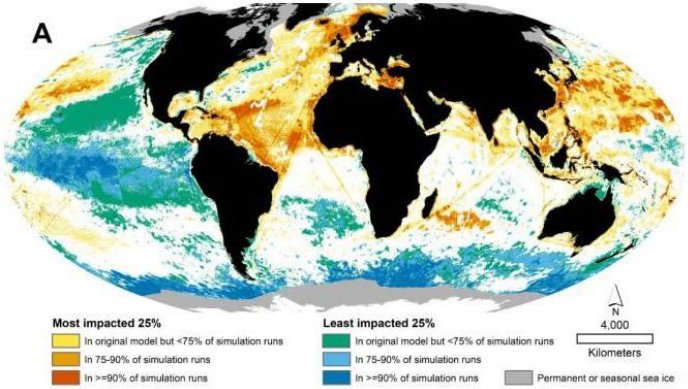
"MC simulation allows for the identification of all the possible outcomes of events, making it easier to assess the impact of risk and allowing for better decision making under uncertain initial conditions."

EY Ernst & Young




Govindarajan Narayanan et al. International Journal of Fatigue, Vol. 83, 2016, 53-58



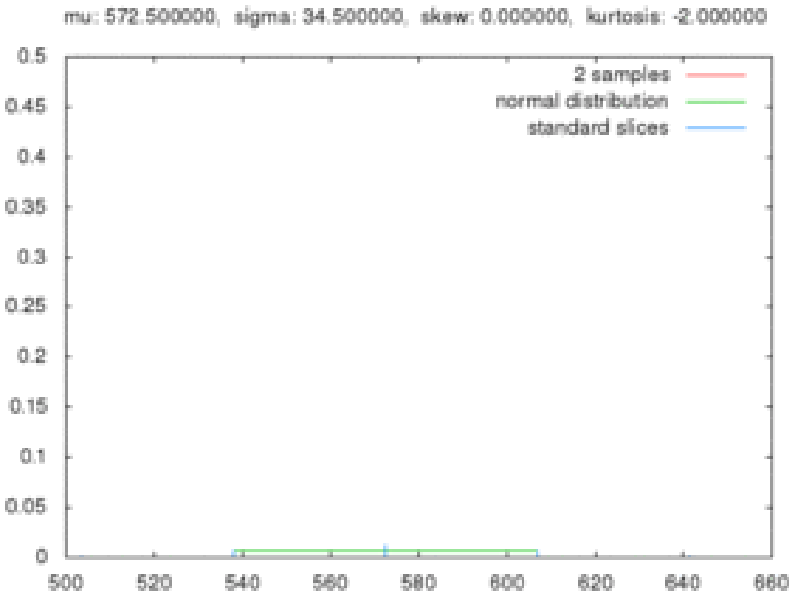

Uncertainty analysis and robust areas of high and low modeled human impact on the global oceans DOI:10.1111/cobi.13141

# Monte Carlo in Materials domain

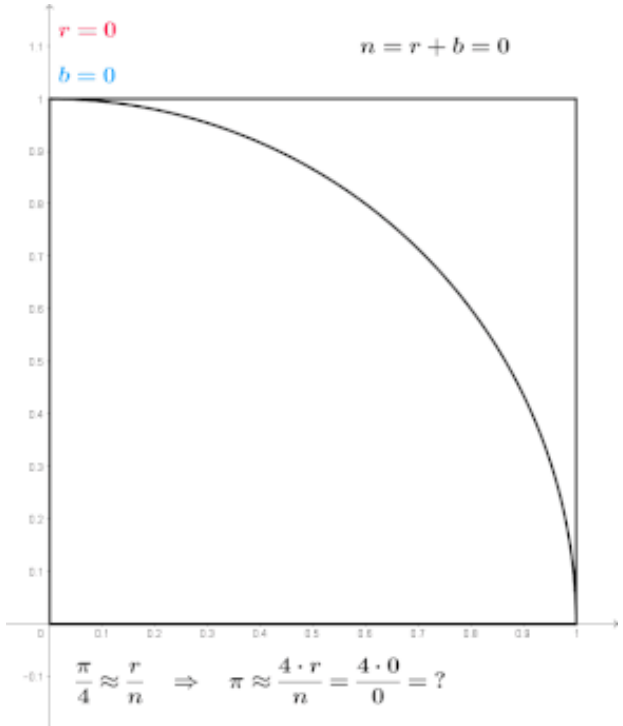
- **Microstructure Modeling** ➔ for e.g., simulate the growth of grain structures in metals.
- **Phase Equilibria** ➔ study phase equilibria in materials, particularly in alloy systems.
- **Defects and Diffusion** ➔ model the behavior of defects such as vacancies, interstitials, and dislocations in crystalline materials. They also help analyze diffusion processes
- **MD Simulations** ➔ phase transitions, and chemical reactions.
- **Electronic Structure Calculations** ➔ often combined with Density Functional Theory (DFT) to understand phase equilibria and calculate electronic properties of materials, including band structures, electronic density of states, and charge distributions.
- **Material Design** ➔ Exploring various atomic configurations and compositions, we can predict how a material will behave under different conditions and tailor its properties accordingly.
- **Material Characterization** ➔ aid in interpreting experimental data, such as X-ray diffraction patterns or nuclear magnetic resonance (NMR) spectra ➔ can help identify the atomic arrangements that best match the observed data, providing valuable insights into the material's structure.
- **Rheology and Mechanical Properties** ➔ study the mechanical properties and rheological behavior of materials, including polymers, composites, and colloidal suspensions. Crucial for engineering applications.
- **Surface and Interface Properties** ➔ Investigate the behavior of materials at surfaces and interfaces. ➔ understand phenomena like surface roughness, adhesion, and the interaction of materials with other substances.

# Example of Monte Carlo Method

- A method to generate random samples to get numerical results.
- We can get results with a certain level of accuracy using MC method

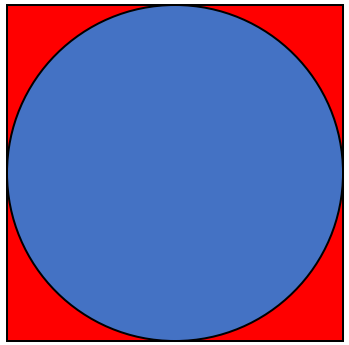



Getting a Normal distribution




Calculating the value of pi

# Simple MC Example: Calculation of π



$$\left.\begin{aligned} A_{\text{square}} &= d^2 \\ A_{\text{circle}} &= \pi d^2 / 4 \end{aligned}\right\} \Rightarrow \pi = 4\frac{A_{\text{circle}}}{A_{\text{square}}}$$

- MC results always good within certain error***, never absolute***!
  Here: Relative error = 1/sqrt(*N*)

- Result:

| | | |
|---|---|---|
| π(10) | = | $4 \pm 1.3$ |
| 100 | = | $3.0 \pm 0.3$ |
| 1000 | = | $3.1 \pm 0.1$ |
| 10,000 | = | $3.13 \pm 0.03$ |
| 100,000 | = | $3.14 \pm 0.01$ |
| 100,000,000 | = | $3.1416 \pm 0.0003$ |
| 1,000,000,000 | = | $3.14158 \pm 0.0001$ |
| | | |
| “real” | | 3.141592654… |

# Thermal averaging: Statistical Mechanics

Statistical Mechanics

| Microscopic (atoms, electrons,…) | Macroscopic Thermodynamics |
| --- | --- |
| Sample with certain constraints | Fixed thermodynamic variable |

Goal: Sample a series of microscopic states that are statistically significant for the long-term averages

# A very brief intro to Statistical Mechanics

*Macroscopic* conditions, such as constant volume, temperature, number of particles, are constraints or boundary conditions to the *microscopic* world.

Microscopic system is defined by the extensive variables that are constant in the macroscopic world. E.g (E, V, N)

The probability distribution for the microscopic system and its Hamiltonian  are related to the macroscopic free energy

# A very brief intro to Statistical Mechanics

The conjugate variable pairs can be identified from the work terms in the first law of thermodynamics

There is one Extensive variable and one Intensive variable

$$dU = TdS + (-pdV) + \mu dN + ...$$

Always need to specify one from each pair

# A very brief intro to Statistical Mechanics

Ensemble is the collection of all possible microscopic states in which the system can be, subject to the thermodynamic (macroscopic) constraints.

E(E,V,N): Micro canonical

E(T,V,N): canonical

E(T,V,$\boldsymbol{\mu}$): grand canonical e.g: open system

# Random (simple) vs Important sampling

Random: Pick M states randomly from ensemble and calculate average property as:

$$\langle A \rangle = \sum_{i=1}^{M} P_i A_i$$

$$P_i = \frac{\exp(-\beta H_i)}{\sum_i^M \exp(-\beta H_i)}$$

Many states with low weights (high energy) will be picked

Probability-weighted sample

$$\langle A \rangle = \sum_{i}^{M} A_i$$

How to construct probability-weighted sample?

# Random vs important sampling

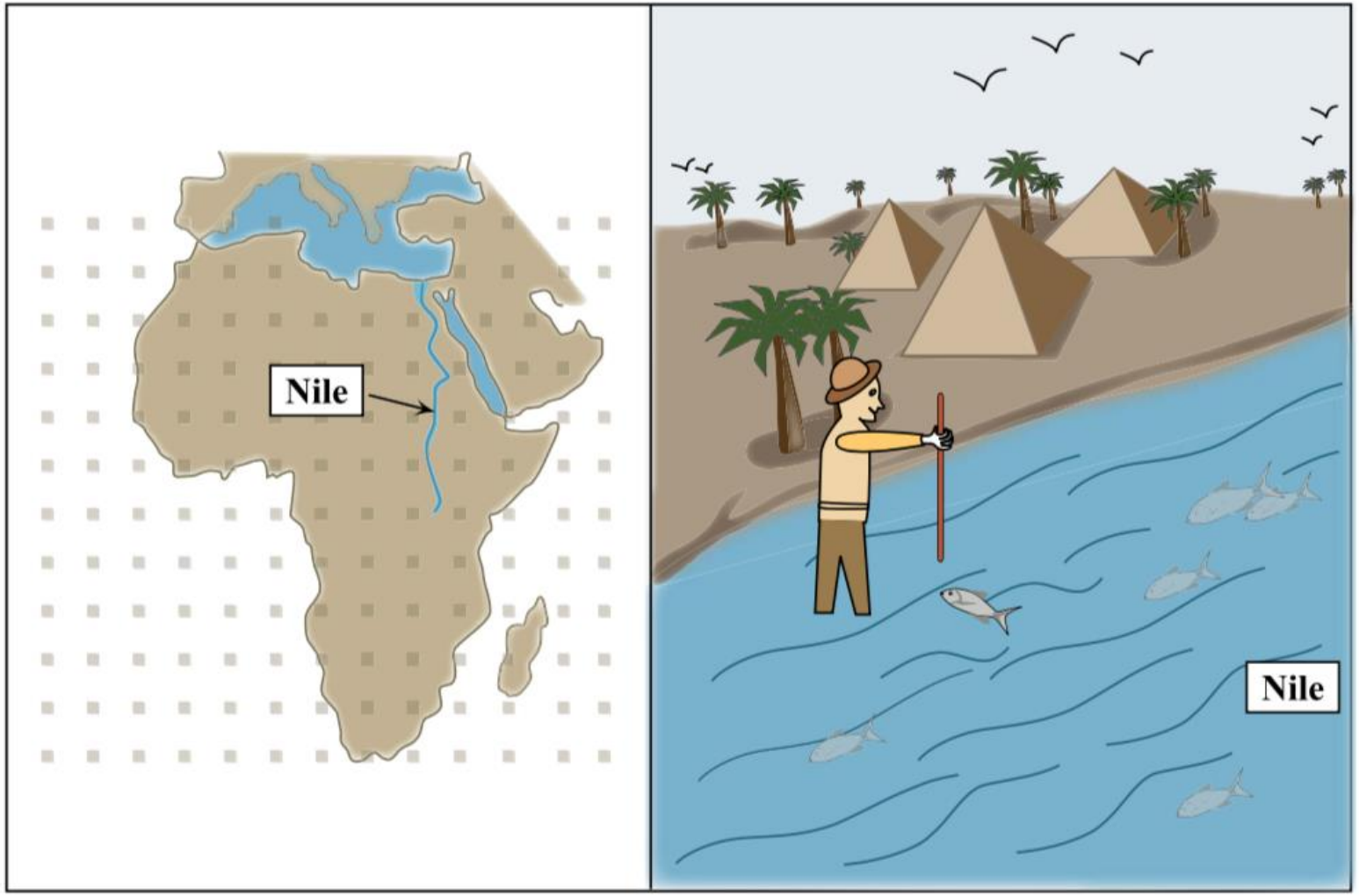



Figure by MIT OCW.

Source: Frenkel, D., and B. Smith. *Understanding Molecular Simulation*. Academic Press.

# Random Sampling and Partition Function

- Thus, Monte Carlo formula to calculate thermal average of *E* is for picking *N* random configurations $C_i$:

$$\langle E \rangle = \frac{1}{N} \frac{\sum_{i=1}^{N} E(C_i) e^{-E(C_i)/kT}}{\sum_{i=1}^{N} e^{-E(C_i)/kT}}$$

Partition function when summed over all N

- ***Problem:*** Most randomly picked configurations $C_i$ will have such high energy that their contribution to sum is negligible $\Rightarrow$ very slow convergence.
- Example for problem size: No of ways to arrange 16 atoms in 8 x 8 lattice

$$N = {}^{64}C_2 \sim 10^{15} \quad \text{configurations}$$

- It will take forever to sample all the configurations. We need to do **Importance Sampling**

# The "Classic" Metropolis method

1. Start with random distribution of atoms A and B on lattice. Calculate the energy for this configuration, $E_1$.
2. Pick one atom A and one B randomly and swap them. Calculate the energy again, $E_2$.
3. Accept the swap with probability

$$P = \begin{cases} 1 \text{ if } E_2 \le E_1 \\ \exp\left(-\dfrac{E_2 - E_1}{k_B T}\right) \text{ otherwise} \end{cases}$$

4. If accepted, the new configuration becomes our starting configuration in 1. Repeat for certain iterations at that temperature

- Temperature selection: Initially high allows easier acceptance of "bad" moves (helps to get out of local minima), then can be lowered to desired value (***"Simulated Annealing"***). **Loop over different temperature from high to low**

# “Accept the Probability” – Enter Randomness

Point 3 of the Metropolis algorithm:

3. Accept the swap with probability

$$P = \begin{cases} 1 \text{ if } E_2 \le E_1 \\ \exp\left( -\dfrac{E_2 - E_1}{k_B T} \right) \text{ otherwise} \end{cases}$$

How?

1. Create random number $x$, $0 \le x < 1$.
2. If $x \le P$, accept. Otherwise, reject.

# Simulated Annealing

- Slowly reduce the temperature of the simulation.
- At the end the system should converge to the global minima.