From Atoms to Materials:
Predictive Theory and Simulations

Week 4: Connecting Atomic Processes to the Macroscopic World
Lecture 4.1: Statistical Mechanics: Connecting the Micro and Macro Worlds

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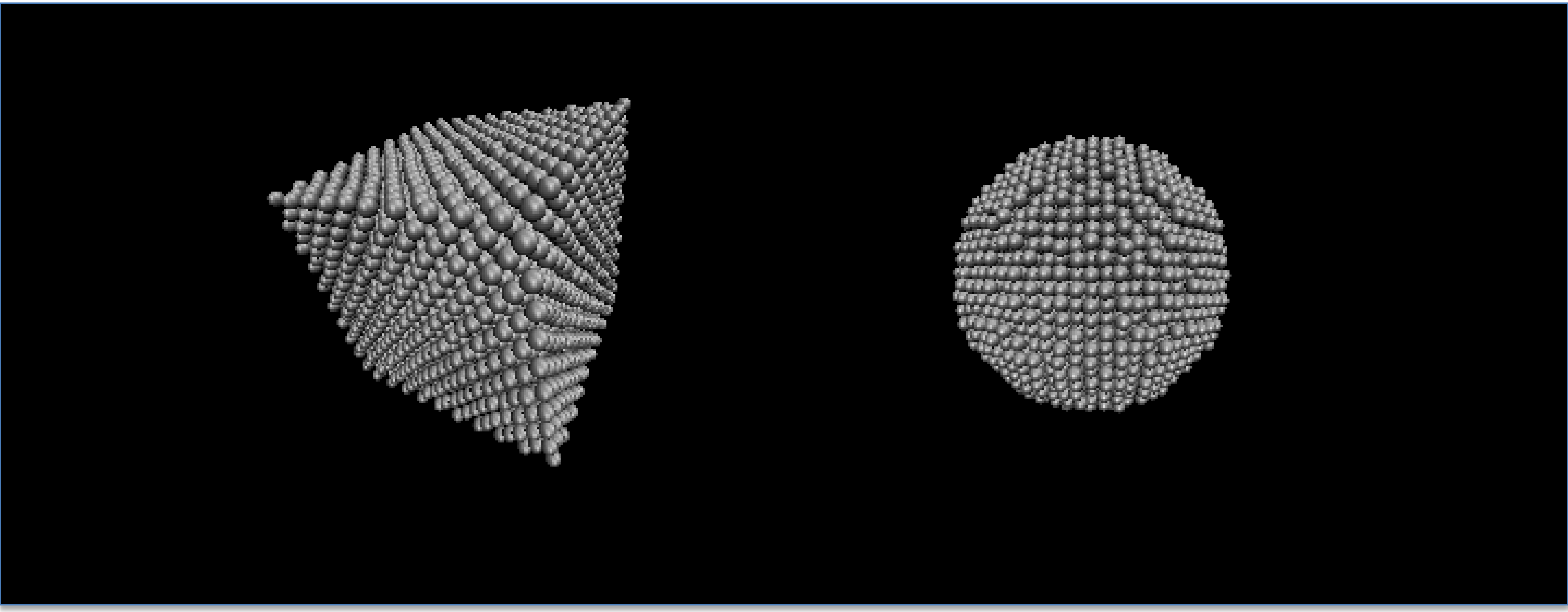
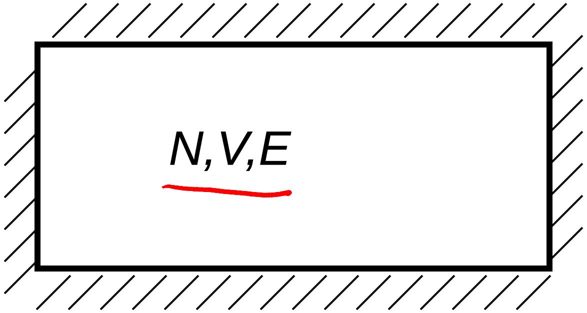
Micro ←→ Macro worlds: statistical mechanics



Relate microscopic phenomena and macroscopic properties

•Given a series of microscopic states, what is the corresponding macroscopic state?
•Given a thermodynamic state of a material, what are the probabilities of finding the system in the various possible microscopic states?

Microscopic probabilities: isolated systems



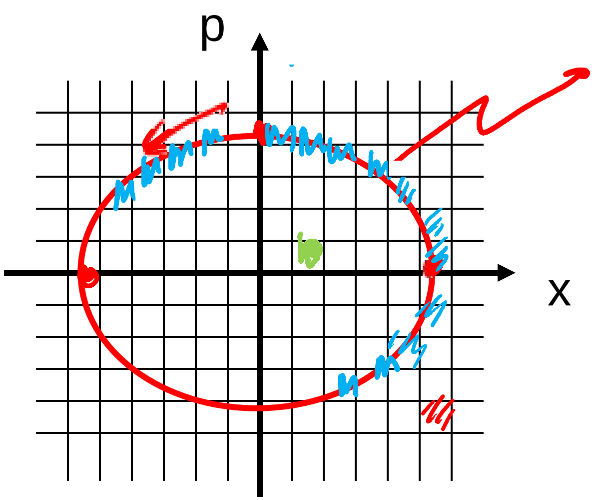
Consider N atoms in a rigid container of volume *V* with constant energy *E*

What is the probability of finding the state in a given microscopic state?

$$\{R_i\} \quad \{P_i\}$$

A simple case: 1-D harmonic oscillator: $H = \dfrac{P^2}{2m} + \dfrac{1}{2} K X^2$

E



$$\Delta x \, \Delta p \geq \hbar$$

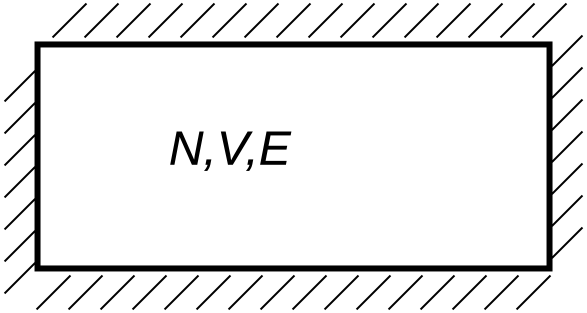
Number of states with energy E:

Dirac's delta

$$\Omega(E) = \frac{1}{\hbar} \int dX\, dP\, \delta\big(E - H(X,P)\big)$$

Equal a-priori probabilities

$N! = N \cdot (N-1) \cdot (N-2) \ldots$



Consider N atoms in a rigid container of volume *V* with constant energy *E*

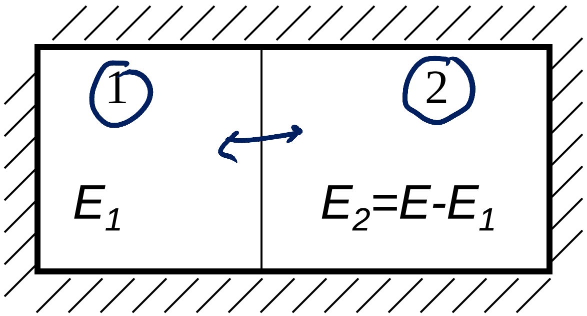
In general: number of different possible microscopic states:

$$\Omega(E,V,N) = \frac{1}{N!\hbar^{3N}} \int_V d^{3N}R \int_{-\infty}^{\infty} d^{3N}P \, \delta\left(H\left(\{R_i\},\{P_i\}\right) - E\right)$$

Postulate: the probability of the material being in any one of the Ω(N,V,E) is the same, i.e. all states are equally likely

$$P(\{R_i\}\{P_i\}) = \begin{cases} 1/\Omega(E,V,N) & \text{if } H(\{R_i\}\{P_i\}) = E \\ 0 & \text{otherwise} \end{cases}$$

Statistical mechanics



- Consider a fictitious separation that divides the material in two subsystems
- Energy can be exchanged between subsystems 1 and 2

•What is the probability of subsystem 1 having energy E_1?

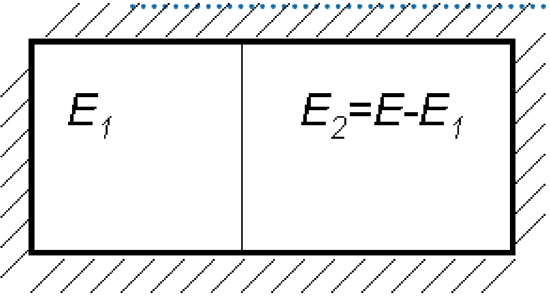
$$P\left(E_1, E-E_1\right)=\frac{\text{Number of microstates with } E_1 \text{ in sub-sys 1}}{\Omega\left(E,V,N\right)}$$

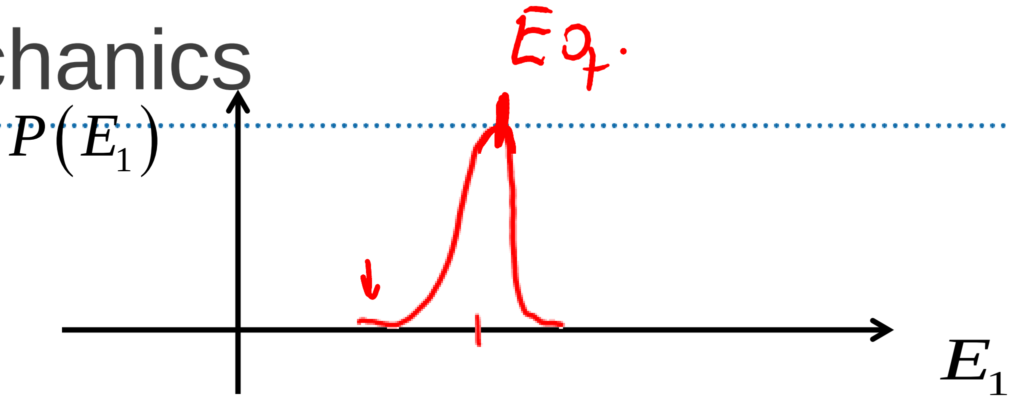
$$P\left(E_1, E-E_1\right)=\frac{\Omega_1\left(E_1,V_1,N_1\right)\cdot\Omega_2\left(E_2,V_2,N_2\right)}{\Omega\left(E,V,N\right)}$$

Additive measure of number of states:

$$\log P\left(E_1, E-E_1\right)=\log\Omega_1\left(E_1,V_1,N_1\right)+\log\Omega_2\left(E-E_1,V-V_1,N-N_1\right)+C$$

Statistical mechanics





- Equilibrium state of the material:
  - Subsystems have the most likely energies: maximum of log$P(E_1,E-E_2)$

$$\frac{\partial \log P(E_1, E-E_1)}{\partial E_1} = 0 = \frac{\partial \log \Omega_1(E_1,V_1,N_1)}{\partial E_1} + \frac{\partial \log \Omega_2(E-E_1,V-V_1,N-N_1)}{\partial E_1}$$

Since E_2=E-E_1: $\frac{\partial}{\partial E_1} = -\frac{\partial}{\partial E_2}$ In equilibrium: $\frac{\partial \log \Omega_1(N_1,V_1,E_1)}{\partial E_1} = -\frac{\partial \log \Omega_2(N_1,V_1,E_1)}{\partial E_2}$

$$\beta(E,V,N) = \frac{\partial \log \Omega(E,V,N)}{\partial E} \qquad \beta_1(E_1,V_1,N_1) = \beta_2(E_2,V_2,N_2)$$

Stat Mech: microcanonical ensemble

*log*Ω is important enough to have its own name: entropy

$$\boxed{S = k \log \Omega(E, V, N)}$$

Temperature:

$$\frac{\partial S(E,V,N)}{\partial E} = \frac{1}{T} \qquad \frac{\partial \Omega(E,V,N)}{\partial E} = \beta = \frac{1}{kT}$$

Pressure:

$$\frac{\partial S(E,V,N)}{\partial V} = -\boxed{\frac{P}{T}}$$

Chemical potential:

$$\frac{\partial S(E,V,N)}{\partial N} = \frac{\mu}{T}$$

Ludwig Boltzmann (1844-1906)

(Image from wikipedia)

Statistical mechanics: further reading

•Kerson Huang: “*Statistical Mechanics*”

•Landau and Lifshitz: “*Course of Theoretical Physics Volume 5: Statistical Physics*”

•Balescu: “*Equilibrium and nonequilibrium statistical mechanics*”