

# ***Purdue MSE597G Lectures on Molecular Dynamics simulations of materials***

## **Lecture 2 Statistical Mechanics I**

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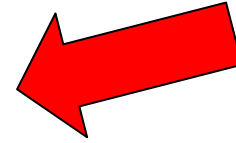
# ***Molecular Dynamics simulations***

## **Introduction**

- What is molecular dynamics (MD)? Examples of current research
- Why molecular dynamics?

## **Part 1: the theory behind molecular dynamics**

- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD



## **Part 2: total energy and force calculations**

- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: “averaging electrons out”

## **Part 3: advanced techniques, mesodynamics, verification and validation**

- MD in under isothermal and isobaric conditions
- Coarse grain approaches and dynamics with implicit degrees of freedom
- Before you perform production runs

- Tutorial to perform MD simulations using the nanoMATERIALS simulation tool at the nanoHUB
- Homework exercises

# ***Analysis/interpretation of MD: statistical mechanics***

Relate microscopic phenomena and macroscopic properties

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

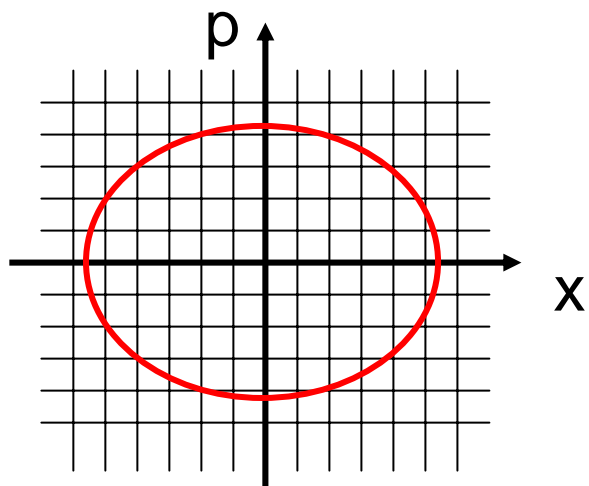
# ***Statistical mechanics***



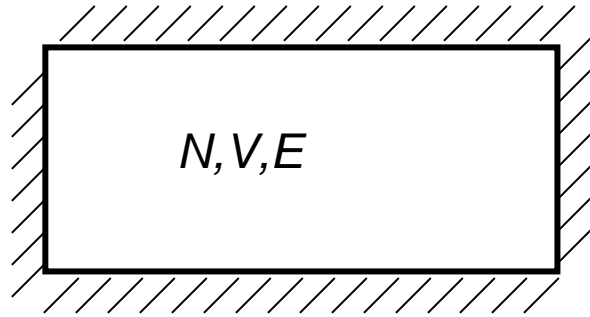
Consider  $N$  atoms in a rigid container of volume  $V$  with constant energy  $E$

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

A simple case: 1-D harmonic oscillator:



# ***Statistical mechanics***

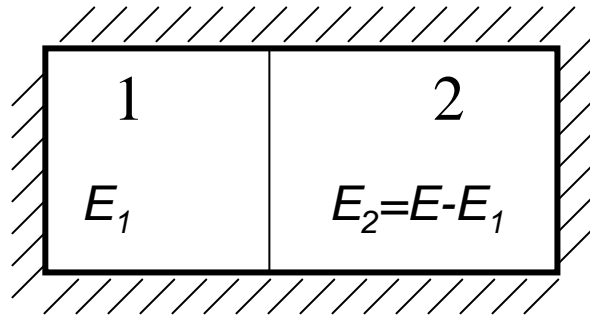


Consider  $N$  atoms in a rigid container of volume  $V$  with constant energy  $E$

Number of different possible microscopic states:

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

# Statistical mechanics



Consider a fictitious separation that divides the material in two subsystems

Energy can be exchanged between subsystems 1 and 2

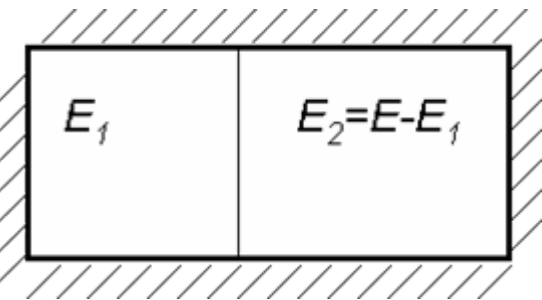
- What is the probability of subsystem 1 having energy  $E_1$ ?

$$P(E_1, E - E_1) = \frac{\text{Number of microstates with } E_1}{\Omega(E, V, N)}$$

Additive measure of number of states:

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

# Statistical mechanics



Equilibrium state of the material:

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

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

# Stat Mech: microcanonical ensemble

$\log \Omega$  is important enough to have its own name: entropy

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

Temperature:

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

Pressure:

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

Chemical potential:

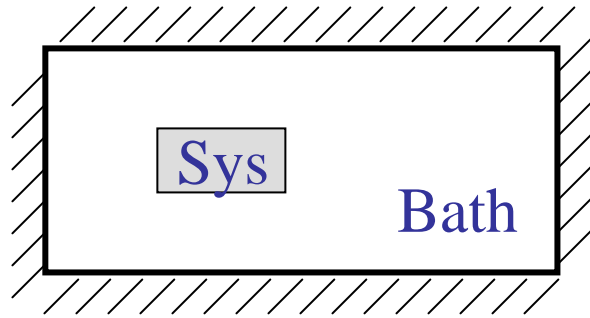
$$\frac{\partial S(E, V, N)}{\partial N} = \frac{\mu}{T}$$

Ludwig Boltzmann (1844-1906)





# Stat Mech: canonical ensemble



$$E + E_{\text{bath}} = E_{\text{tot}} = \text{Constant}$$

Probability of system being in a **microscopic**  $(\{r_i\}, \{p_i\})$  state with energy  $E$ :

$$P(\{r_i\}, \{p_i\}) = \frac{\Omega_{\text{bath}}(E_{\text{tot}} - H(\{r_i\}, \{p_i\}))}{\Omega_{\text{total}}}$$

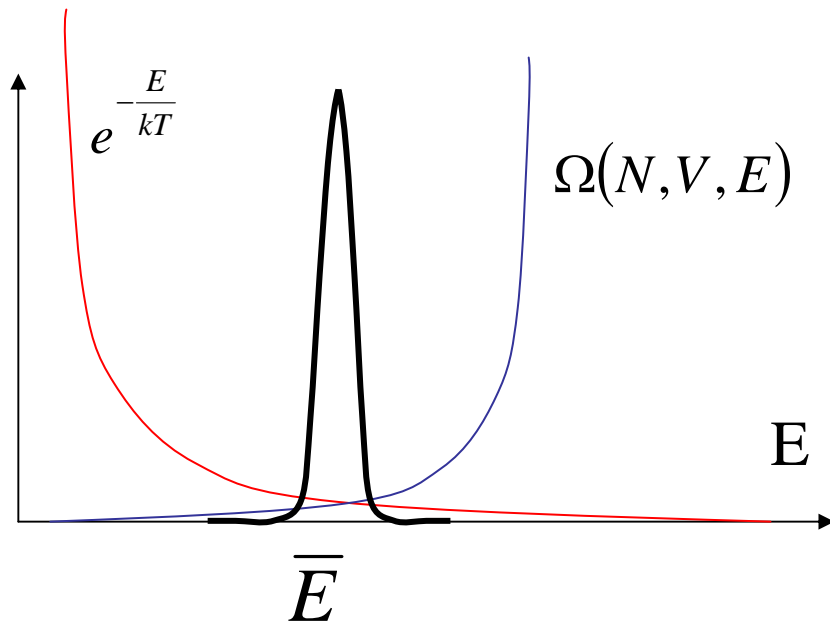
Since  $E \ll E_{\text{tot}}$  we expand  $\log \Omega_{\text{bath}}$  around  $E_{\text{tot}}$ :

# Canonical ensemble and thermodynamics

Maxwell-Boltzmann distribution  $P(\{r_i\}, \{p_i\}) = \frac{e^{-\beta H(\{r_i\}, \{p_i\})}}{\sum_{\text{microstates}} e^{-\beta H(\{r_i\}, \{p_i\})}}$

Partition function:  $Z(N, V, T) = \sum_{\text{microstates}} e^{-\beta H(\{r_i\}, \{p_i\})}$

$$Z(N, V, T) = \sum_E \Omega(N, V, E) e^{-\frac{E}{kT}} = \Omega(N, V, \bar{E}) e^{-\frac{\bar{E}}{kT}}$$



$$\log Z(N, V, T) = \log \Omega(N, V, E) - \frac{E}{kT}$$

Helmholtz free energy:

$$F = E - TS = -kT \log Z(N, V, T)$$

# Canonical ensemble: averages

Consider a quantity that depends on the atomic positions and momenta:

$$A(\{r_i\}, \{p_i\})$$

In equilibrium the average values of A is:

$$\langle A \rangle = \sum_{microstates} A P_{micro} = \frac{\sum_{microstates} A(\{r_i\}, \{p_i\}) e^{-\beta H(\{r_i\}, \{p_i\})}}{\sum_{microstates} e^{-\beta H(\{r_i\}, \{p_i\})}} \quad \text{Ensemble average}$$

When you measure the quantity A in an experiment or MD simulation:

$$\frac{1}{\tau} \int_0^{\tau} dt A(\{r_i(t)\}, \{p_i(t)\}) \quad \text{Time average}$$

Under equilibrium conditions temporal and ensemble averages are equal

# Canonical ens.: equipartition of energy

Consider a variable that appears squared in the Hamiltonian:

$$H(\{r_i\}, \{p_i\}) = \lambda p_1^2 + V(\{r_i(t)\}) + \sum_{i=2}^{3N} \frac{p_i(t)^2}{2m_i} = \lambda p_1^2 + H'$$

$$\langle \lambda p_1^2 \rangle = \frac{\int d^{3N} p \, d^{3N} p \, \lambda p_1^2 e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}}{\int d^{3N} p \, d^{3N} p e^{-\frac{H(\{r_i\}, \{p_i\})}{kT}}} = \frac{\int d^{3N} p \, d^{3N-1} p e^{-\frac{H'}{kT}} \int dp_1 \lambda p_1^2 e^{-\frac{\lambda p_1^2}{kT}}}{\int d^{3N} p \, d^{3N-1} p e^{-\frac{H'}{kT}} \int dp_1 e^{-\frac{\lambda p_1^2}{kT}}}$$

Change of variable:  $\frac{\lambda p_1^2}{kT} = x^2 \quad dp_1 = \frac{kT}{\lambda} dx$

$$\langle \lambda p_1^2 \rangle = \frac{\frac{(kT)^2}{\lambda} \int dx \, x^2 e^{-x^2}}{\frac{kT}{\lambda} \int dx e^{-x^2}} = \frac{1}{2} kT$$

**Equipartition of energy:** Any degree of freedom that appears squared in the Hamiltonian contributes  $1/2kT$  of energy