CHM 421/621
Statistical Mechanics

Lecture 21 Microcanonical Ensemble Examples - 2

Formalisms of Statistical Mechanics

Lecture Plan

Basic Postulates

Counting microstates in an ideal gas

Boltzmann equation for entropy

Microcanonical Ensemble

Canonical Ensemble

Formalisms of Statistical Mechanics

Boltzmann equation for entropy

Simple Harmonic Oscillator

Consider a system of N quantum oscillators having a total energy U and a fundamental frequency ω.

Eigenvalues for each oscillator $$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

Total energy:

$$\begin{aligned} E^\mu &= \sum_{i=1}^{N}\left(n_i^\mu + \frac{1}{2}\right)\hbar\omega \\ &= \left(\sum_{i=1}^{N} n_i^\mu\right)\hbar\omega + \frac{N}{2}\hbar\omega \\ &\equiv N^\mu \hbar\omega + U_0/2 \end{aligned}$$

Taking $U_0/2$ as a reference energy the total number of quanta can be written as

$$N^\mu = \frac{U}{\hbar\omega}$$

Formalisms of Statistical Mechanics

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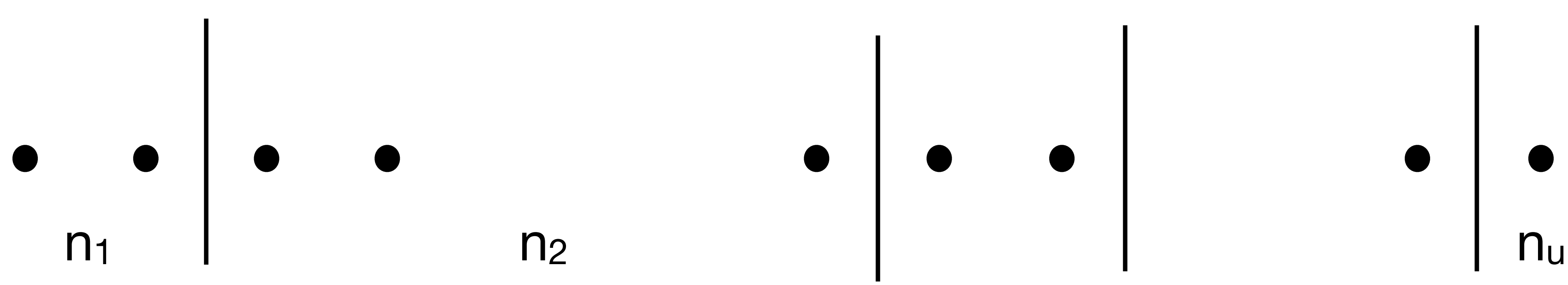
The number of microstates possible for a given energy *U* is just the number of ways of partitioning N^{μ} into *N* parts such that:

$$\sum_{i=1}^{N} n_i^{\mu} = N^{\mu}$$

This problem is isomorphic to finding ways of making *N-1* partitions separating N^{μ} points.



Formalisms of Statistical Mechanics

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Simple Harmonic Oscillator

Given that the partitions are identical and the points are identical we have

$$\Omega = \frac{(N^\mu + N - 1)!}{N^\mu!\,(N-1)!} \approx \frac{(N^\mu + N)!}{N^\mu! N!} \qquad (N \to \infty)$$

$$\begin{aligned}
S &= k_B \ln \Omega(U, V, N) \\
&= k_B \left[(N^\mu + N) \ln(N^\mu + N) - (N^\mu + N) - (N^\mu \ln N^\mu - N^\mu + N \ln N - N) \right] \\
&= k_B \left[N^\mu \ln\left(1 + \frac{N}{N^\mu}\right) + N \ln\left(1 + \frac{N^\mu}{N}\right) \right] \\
&= N k_B \left[\frac{U}{U_0} \ln\left(1 + \frac{U}{U_0}\right) + \ln\left(1 + \frac{U}{U_0}\right) \right]
\end{aligned}$$

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Given that the partitions are identical and the points are identical we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{k_B}{\hbar\omega_0} \ln\left(1 + \frac{N}{U}\hbar\omega_0\right)$$

Average energy per oscillator is

$$u = \frac{\hbar\omega_0}{e^{\frac{T_E}{T}} - 1} \qquad T_E = \frac{\hbar\omega_0}{k_B}$$

Einstein temperature

Formalisms of Statistical Mechanics

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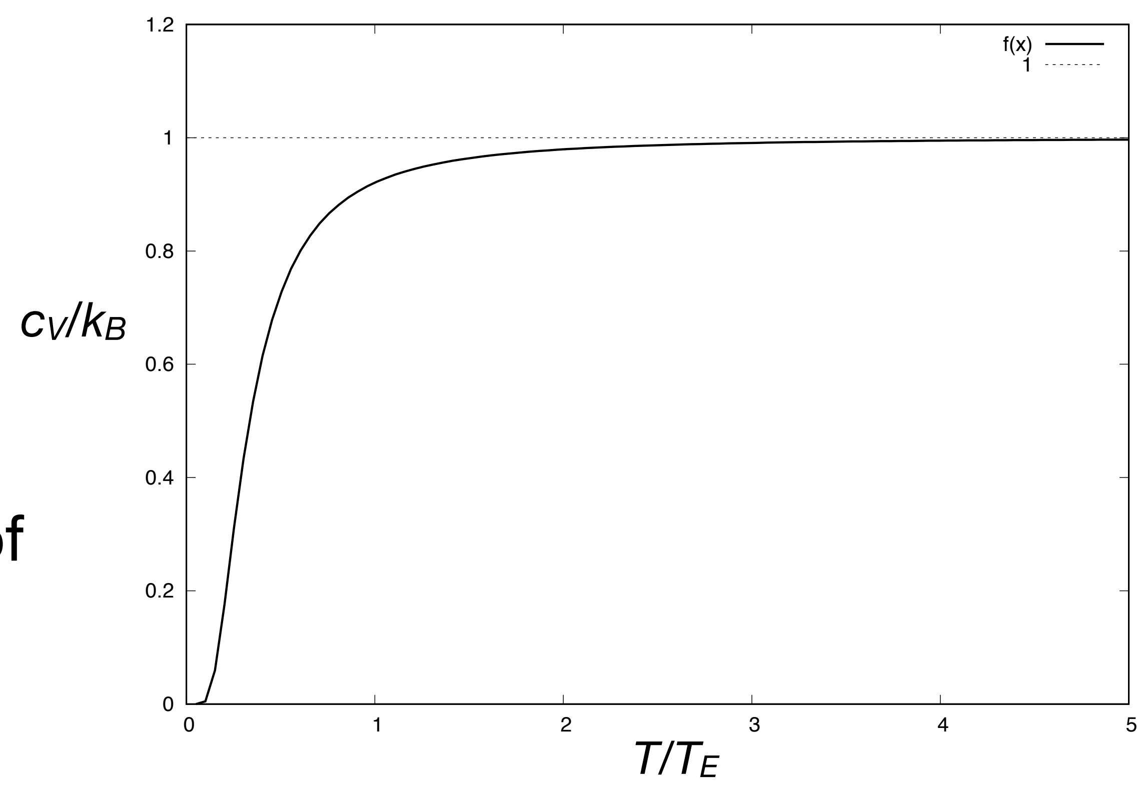
<u>Simple Harmonic Oscillator</u>

Specific heat

$$c_V = k_B \left(\frac{T_E}{T}\right)^2 \frac{e^{\frac{T_E}{T}}}{\left(e^{\frac{T_E}{T}} - 1\right)^2}$$



Such a model was used by Einstein to account for the specific heat of solids.

Ensembles

Microcanonical Ensemble

A collection of identical isolated systems with the same energy *U*.

Each system can be thought of realising one of the possible microstates consistent with the *a priori* probabilities.

Then the fraction of systems corresponding to a particular microstate is equal to $1/\Omega$