

MSAE3111, Thermodynamics and Statistical Mechanics

Prof. William Bailey

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The problem

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The
Boltzmann
factor

- Two states (1, 2)

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- $E_2 - E_1 = \Delta E_{12} > 0$

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- *Singly occupied*: ($N = 1$).

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 - $E_2 - E_1 = \Delta E_{12} > 0$
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-
- **Question**: how much more probable for 1 to be occupied than 2 at temperature T ?

We divide the universe

- Two regions:

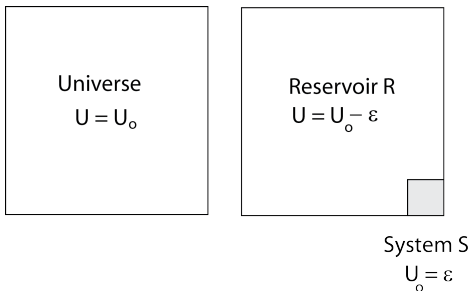


Figure: Universe: tiny system, big reservoir.

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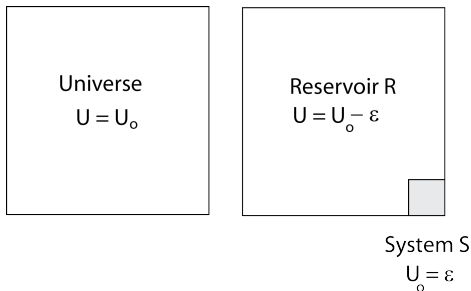


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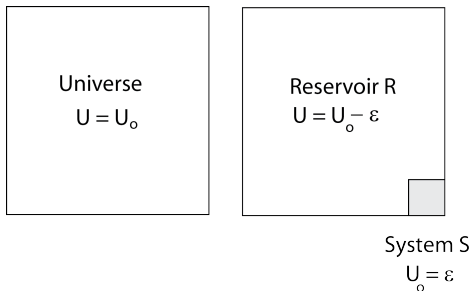


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- *System S*
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Interested in understanding the system.

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Energy: $U_{\mathcal{S}} = \epsilon$

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All parts of the universe which are not the system.

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All parts of the universe which are not the system.

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- Total energy $U_0 = U_{\mathbb{S}} + U_{\mathbb{R}}$

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- Total energy $U_0 = U_{\mathbb{S}} + U_{\mathbb{R}}$

$\Rightarrow U_{\mathbb{R}} = U_0 - \epsilon$

Evaluating multiplicity

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- multiplicity of the whole universe

$$g_{tot} = g^S g^R \quad (1)$$

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$$g_{tot} = g^{\mathbb{S}} g^{\mathbb{R}} \quad (1)$$

- *Taking \mathbb{S} as a single state:*

$$g^{\mathbb{S}} = 1.$$

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$$g_{tot} = g^{\mathbb{S}} g^{\mathbb{R}} \quad (1)$$

- *Taking \mathbb{S} as a single state:*

$$g^{\mathbb{S}} = 1.$$

- Total multiplicity is multiplicity of reservoir \mathbb{R}

$$g_{tot} = g^{\mathbb{R}} \quad (2)$$

Evaluating multiplicity

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- *Different states: 1 and 2*

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- *Different states:* 1 and 2
- *Different energies:* ϵ_1 , ϵ_2 .

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$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{g(\epsilon_1)}{g(\epsilon_2)} \quad (3)$$

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- In terms of reservoir \mathbb{R}

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \frac{g^{\mathbb{R}}(U_o - \epsilon_1)}{g^{\mathbb{R}}(U_o - \epsilon_2)} \quad (4)$$

Evaluating multiplicity

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- From $\sigma = \ln g$,

$$\frac{P(\epsilon_1)}{P(\epsilon_2)} = \exp \sigma^{\mathbb{R}}(U_o - \epsilon_1) - \sigma^{\mathbb{R}}(U_o - \epsilon_2) \quad (5)$$

Evaluating multiplicity

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- expand $\sigma(U_o - \epsilon)$, $\epsilon \ll U_o$ —system is tiny

$$\sigma(U_o - \epsilon) \simeq \sigma(U_o) - \epsilon \frac{\partial \sigma}{\partial \epsilon}(U_o) \dots \quad (6)$$

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- but from

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (7)$$

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- but from

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (7)$$

- we have

$$\left(\frac{\partial \sigma}{\partial \epsilon}\right) = \frac{1}{k_B T} \quad (8)$$

Evaluating multiplicity

- but from

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (7)$$

- we have

$$\left(\frac{\partial \sigma}{\partial \epsilon}\right) = \frac{1}{k_B T} \quad (8)$$

- Finally:

$$\frac{P(E_2)}{P(E_1)} = e^{\frac{-\Delta E}{k_B T}} \quad (9)$$

Two-level system

- See plot:

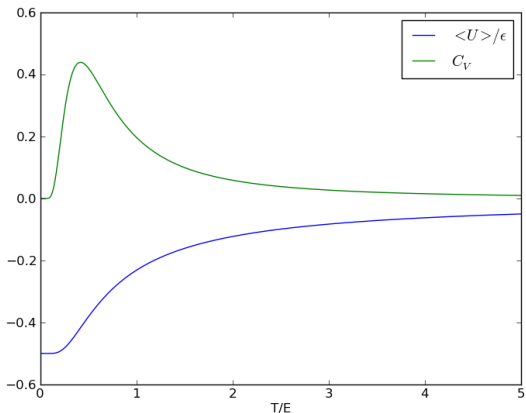


Figure: Heat capacity and average energy for a two-level