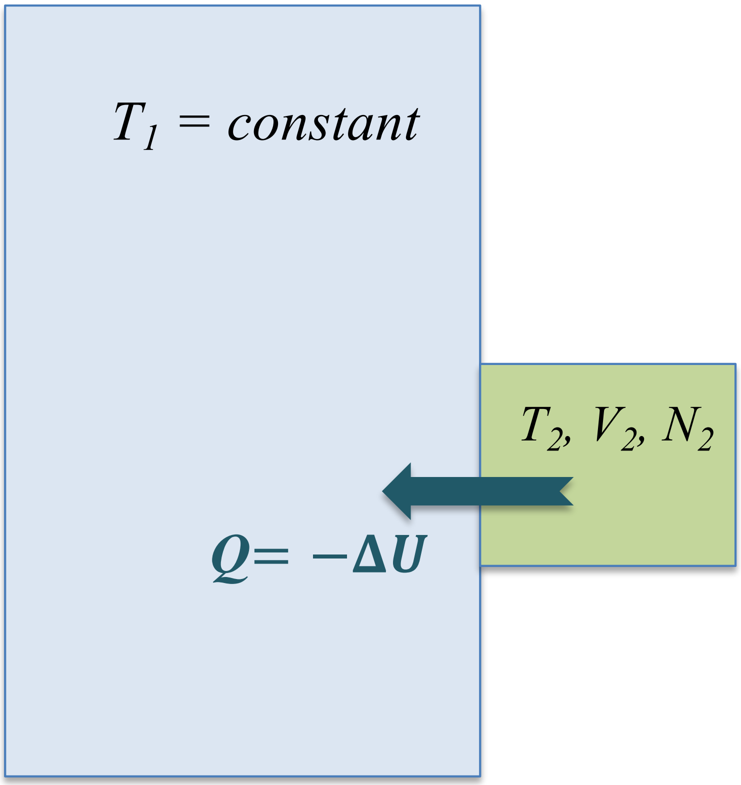
Notes:

I showed these few slides as introduction to the partition function; but they are now corrected to show our current notation for the internal energy, U.

Canonical Ensemble:

System of interest at constant *T*, in equilibrium with heat bath.
Very large reservoir: *T* doesn't change



Recall, *S maximized* (for entire system); occurs by spontaneous processes while approaching equilibrium

At equilibrium, 2 sides can exchange small amounts of energy.
Consider 2 specific microstates in system 2:

$$\frac{P_A}{P_B} = e^{[S_R(A) - S_R(B)]/k_B} = e^{-\Delta U/k_B}$$

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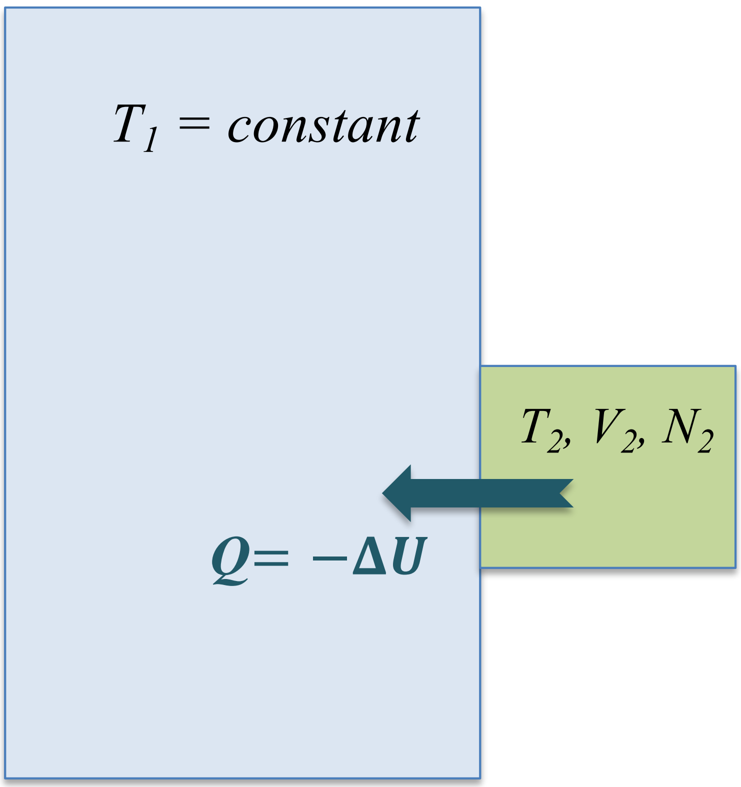

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Probability of finding system in state *i* in equilibrium

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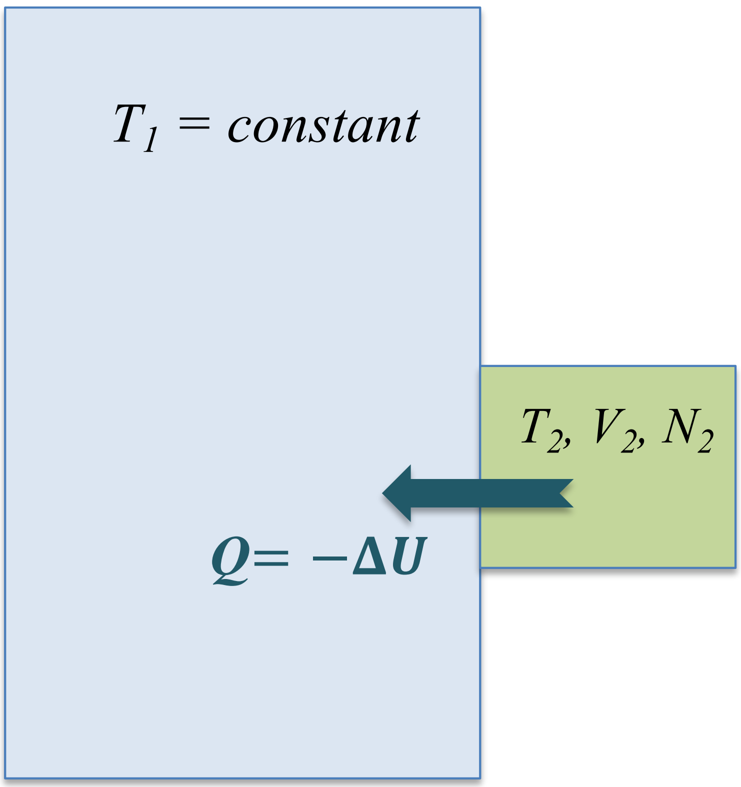

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Boltzmann distribution

$$P_i = \frac{1}{Z} e^{-E_i/kT}$$

Partition function

$$Z = \sum_{states\ i} Exp[-E_i/kT]$$

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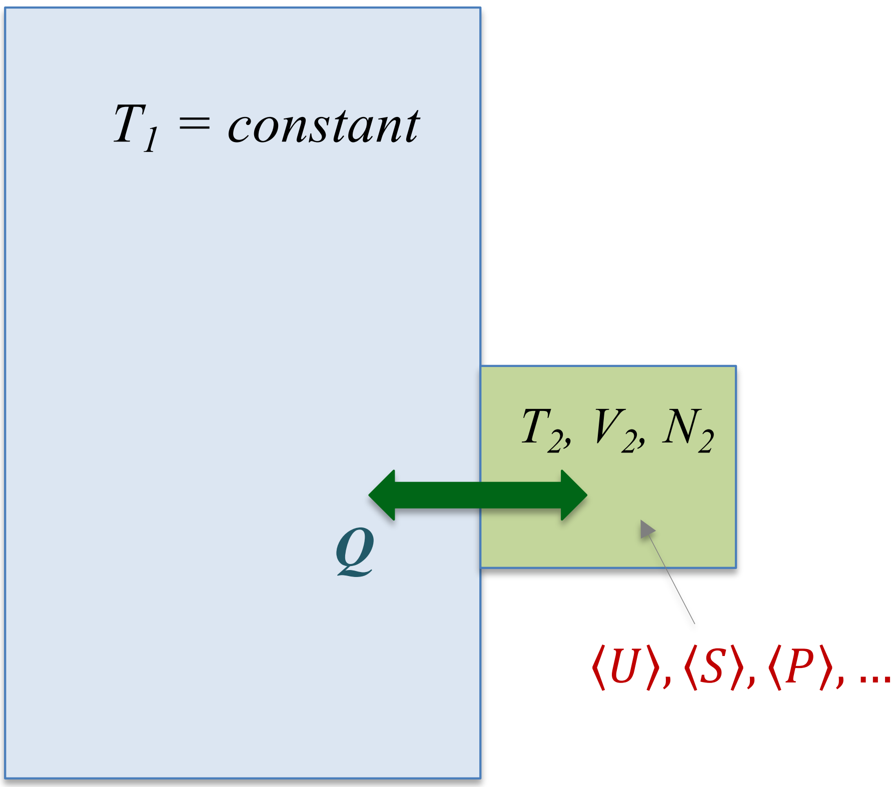

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Probability of finding system in state *i* in equilibrium

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Partition function

probabilistic interpretation of system 2's energy, entropy, etc.

(Valid for small or large systems; fluctuations vanish in large-size limit.)

Sum over microstates:

- Classical systems: integral over phase space
- Quantum 1-particle systems: sum over single-particle energy states.
- In general, sum over all eigenstates.

Some Results:

$$\beta = \frac{1}{kT}$$

- Energy averaging

$$E_i \rightarrow \langle E \rangle = U = -\frac{\partial}{\partial \beta} lnZ \qquad = kT^2 \frac{\partial}{\partial T} lnZ$$

(average *E* equivalent to fixed energy *U* in thermodynamic limit)

Also can show, energy *fluctuations* vanish in thermodynamic limit.

- ▻ Works for finite system contacting reservoir, even though reservoir is infinitely large.
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$$\Delta E_{rms} = (\langle E^2 \rangle - \langle E \rangle^2)^{1/2}$$

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} Z \qquad \frac{\partial^2}{\partial \beta^2} \ln Z = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 = \langle E^2 \rangle - \langle E \rangle^2$$

Result:

$$\frac{\Delta E_{rms}}{E} = \left| \frac{\partial \langle E \rangle}{\partial \beta} \right|^{1/2} \Big/ \langle E \rangle \sim 1/\sqrt{N} \rightarrow 0$$

typical, not always