Equilibrium in Constant T

Thermodynamics

Constant U Equilibrium

Constant T Equilibrium

Constructing Our Equilibrium

Maximize S

Minimize F

Statistical Mechanics

Constant U Equilibrium

Constant T Equilibrium

Counting Available Microstates

$\Omega(U)$

?

Constructing Our Equilibrium

$S = k\ln\Omega$

Maximize S

?

Our partition function scales with the number of available states.

$$Z = \sum e^{-\beta E_s} = \sum e^{-\frac{E_s}{kT}}$$

$$E_s \ll kT$$

$$Z = \Omega$$

$$E_s \gg kT$$

$$Z = e^{-\frac{E_0}{kT}}$$

Statistical Mechanics

Constant U Equilibrium

Constant T Equilibrium

Counting Available Microstates

$\Omega(U)$

$Z(T)$

Constructing Our Equilibrium

$S = k\ln\Omega$

?

Maximize S

$$Z = \sum e^{-\beta E_s} = \sum e^{-\frac{E_s}{kT}}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

Remember that we figured out this useful relationship between S and F!

$$F_{ig} = -k\ln Z$$

A reasonable guess would be to parallel our stat mech S formula.

$$F = -kT\ln Z$$

We know the units of F, so we can make our guess better by adding in a T.

$$Z = e^{-\frac{F}{kT}}$$

Statistical Mechanics

Constant U Equilibrium		Constant T Equilibrium
↓	Counting Available Microstates	↓
Ω(U)		Z(T)
↓	Constructing Our Equilibrium	↓
$S = k\ln\Omega$		$F = -kT\ln Z$
Maximize S		Minimize F

Thermo

$$F = U - TS \longrightarrow -S = \frac{F-U}{T}$$

Stat Mech

$$F = -kT\ln Z$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T}$$

Let's prove it!
First, I will show both formulations of F obey the same differential equation. Then, I will show that the two solutions are identical because they satisfy boundary conditions. Then I will have shown that these two formulations of F are equivalent.

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T}$$

$$Z = \sum e^{-\beta E_s} = \sum e^{-\frac{E_s}{kT}}$$

$$\tilde{F} = -kT\ln Z$$

$$\frac{\partial}{\partial T}(-kT\ln Z(T))_{V,N} = -k\ln Z - kT\frac{\partial}{\partial T}(\ln Z)$$

$$\frac{\partial}{\partial T}(\ln Z) = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta}(\ln Z)$$

$$= -\frac{1}{kT^2}\frac{\partial}{\partial \beta}(\ln Z)$$

$$= -\frac{1}{kT^2}\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= \frac{U}{kT^2}$$

$$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{V,N} = -k\ln Z - \frac{U}{T}$$

$$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{V,N} = -k\ln Z - \frac{U}{T}$$

$$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{V,N} = \frac{-kT\ln Z - U}{T}$$

$$\left(\frac{\partial \tilde{F}}{\partial T}\right)_{V,N} = \frac{\tilde{F} - U}{T}$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F - U}{T}$$

$$\tilde{F} = -kT\ln Z$$

They have the same differential equation!

Now let's check boundary conditions

$$F = U - TS$$

$$F(T = 0) = U_0$$

$$\tilde{F} = -kT\ln Z$$

$$\tilde{F}(T = 0) = -kT\ln(e^{-\frac{U_0}{kT}})$$

$$\tilde{F}(T = 0) = U_0$$

$$E_s \gg kT$$

$$Z = e^{-\frac{E_0}{kT}}$$

$$F = \tilde{F}$$

$$F = -kT\ln Z$$

Statistical Mechanics

Constant U Equilibrium

Constant T Equilibrium

Counting Available Microstates

$\Omega(U)$ → $Z(T)$

Constructing Our Equilibrium

$S = k\ln\Omega$

$F = -kT\ln Z$

Maximize S

Minimize F

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \qquad \mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

Consider a collection of N identical harmonic oscillators (like an Einstein solid), in thermal contact with a reservoir and held at constant temperature T. The allowed energies for such a system are 0, hf, 2hf, ...
Find expressions for S(T), U(T).
1st: Find Z

$$Z = \sum e^{-\beta E_s} = \sum e^{-\frac{E_S}{kT}}$$

$$Z = 1 + e^{-\beta hf} + e^{-2\beta hf} + ...$$

$$Z = 1 + x + x^2 + ...$$

$$Z = \frac{1}{1-x}$$

$$Z = \frac{1}{1 - e^{-\beta hf}}$$

2nd: Find F

$$F = -kT\ln Z$$

$$F = -kT\ln\left(\frac{1}{1-e^{-\beta hf}}\right)$$

$$F = kT\ln(1-e^{-\beta hf})$$

3rd: Construct S(T)

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = k\ln(1-e^{-\beta hf}) + \frac{kT}{1-e^{-\beta hf}}\left(\frac{hf}{kT^2}e^{-\beta hf}\right)$$

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = k\ln(1-e^{-\beta hf}) + \frac{hfe^{-\beta hf}}{T(1-e^{-\beta hf})} = -S(T)$$

$$F = kT\ln(1 - e^{-\beta hf})$$

4th: Construct U

$$F = U - TS$$

$$F = -kT\ln Z$$

$$S = -k\ln(1 - e^{-\beta hf}) - \frac{hfe^{-\beta hf}}{T(1 - e^{-\beta hf})}$$

$$kT\ln(1 - e^{\beta hf}) = U + kT\ln(1 - e^{-\beta hf}) + \frac{hfe^{-\beta hf}}{1 - e^{-\beta hf}}$$

$$U = \frac{hfe^{-\beta hf}}{e^{-\beta hf} - 1}$$

Statistical Mechanics

Constant U Equilibrium		Constant T Equilibrium
↓	Counting Available Microstates	↓
Ω(U)		Z(T)
↓	Constructing Our Equilibrium	↓
S = klnΩ		F = -kTlnZ
Maximize S		Minimize F

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \qquad \mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}.$$