HW#8

8.1

(a)

The system has two energy states $(0, \varepsilon)$, the accessible states are below.

State number	Description	N	Energy
1	(0, 0)	0	0
2	(1, 0)	1	0
3	(0, 1)	1	ε

Thus, the Gibbs sum is

$$Z = \exp(0/\tau) + \exp(\mu/\tau) + \exp[(\mu-\varepsilon)/\tau]$$
$$= 1 + \lambda + \lambda \exp(-\varepsilon/\tau)$$

(b)

$$< N >= \frac{0\times 1 + 1\times\lambda + 1\times\lambda\exp(-\varepsilon/\tau)}{Z} = \frac{\lambda + \lambda\exp(-\varepsilon/\tau)}{Z}$$

(c)

At energy ε, we just need the last term in the expression for <N>

$$< N(\varepsilon) >= \frac{1\times\lambda\exp(-\varepsilon/\tau)}{Z} = \frac{\lambda\exp(-\varepsilon/\tau)}{Z}$$

(d)

The thermal average energy is

$$< U >= \frac{0\times 1 + 0\times\lambda + \varepsilon\times\lambda\exp(-\varepsilon/\tau)}{Z} = \frac{\varepsilon\lambda\exp(-\varepsilon/\tau)}{Z}$$

(e)

In this case, the accessible states are below.

State number	Description	N	Energy
1	(0, 0)	0	0
2	(1, 0)	1	0
3	(0, 1)	1	ε
4	(1, 1)	2	ε

Thus, the Gibbs sum is

$$Z = \exp(0/\tau) + \exp(\mu/\tau) + \exp[(\mu-\varepsilon)/\tau] + \exp[(2\mu-\varepsilon)/\tau]$$
$$= 1 + \lambda + \lambda\exp(-\varepsilon/\tau) + \lambda^2\exp(-\varepsilon/\tau)$$
$$= (1+\lambda)[1+\lambda\exp(-\varepsilon/\tau)]$$

8.2

(a)

We have the Gibbs sum is

$$Z = 1 + \lambda(O_2)\exp(-\varepsilon_A/\tau) + \lambda(CO)\exp(-\varepsilon_B/\tau)$$

When consider the system in the absence of CO, we have

$$Z = 1 + \lambda(O_2)\exp(-\varepsilon_A/\tau)$$

$$\frac{\lambda(O_2)\exp(-\varepsilon_A/\tau)}{1+\lambda(O_2)\exp(-\varepsilon_A/\tau)}=0.9$$

$$\Rightarrow \lambda(O_2)\exp(-\varepsilon_A/\tau)=9$$

$$\Rightarrow \exp(-\varepsilon_A/\tau)=9\times 10^5$$

$$\Rightarrow -\varepsilon_A/\tau=13.71$$

$$\Rightarrow \varepsilon_A=-13.71\times k_B T=-13.71\times 8.617\times 10^{-5} eV/K\times 310.15K=-0.366eV$$

(b)

In this case, we have

$$\frac{\lambda(O_2)\exp(-\varepsilon_A/\tau)}{1+\lambda(O_2)\exp(-\varepsilon_A/\tau)+\lambda(CO)\exp(-\varepsilon_B/\tau)}=0.1$$

$$\Rightarrow \frac{9}{10+\lambda(CO)\exp(-\varepsilon_B/\tau)}=0.1$$

$$\Rightarrow \lambda(CO)\exp(-\varepsilon_B/\tau)=80$$

$$\Rightarrow \exp(-\varepsilon_B/\tau)=8\times 10^8$$

$$\Rightarrow -\varepsilon_B/\tau=20.5$$

$$\Rightarrow \varepsilon_B=-20.5\times k_B T=-20.5\times 8.617\times 10^{-5} eV/K\times 310.15K=-0.548eV$$

8.3

(a)

From (6.4), we have

$$f(\varepsilon)=\frac{1}{\exp[(\varepsilon-\mu)/\tau]+1}$$

$$\Rightarrow \frac{\partial f}{\partial \varepsilon}=-\frac{1}{\{\exp[(\varepsilon-\mu)/\tau]+1\}^2}\times\exp[(\varepsilon-\mu)/\tau]\times 1/\tau$$

$$=-\frac{\exp[(\varepsilon-\mu)/\tau]}{\tau\{\exp[(\varepsilon-\mu)/\tau]+1\}^2}$$

When $\varepsilon=\mu$, we have

$$\exp[(\varepsilon-\mu)/\tau]=1$$

$$\Rightarrow -\frac{\partial f}{\partial \varepsilon}=\frac{1}{4\tau}$$

(b)

$$f(\mu+\delta)=\frac{1}{\exp[(\mu+\delta-\mu)/\tau]+1}=\frac{1}{\exp(\delta/\tau)+1}$$

$$f(\mu-\delta)=\frac{1}{\exp[(\mu-\delta-\mu)/\tau]+1}=\frac{1}{\exp(-\delta/\tau)+1}=\frac{\exp(\delta/\tau)}{\exp(\delta/\tau)+1}$$

$$\Rightarrow f(\mu+\delta)+f(\mu-\delta)=\frac{1}{\exp(\delta/\tau)+1}+\frac{\exp(\delta/\tau)}{\exp(\delta/\tau)+1}=1$$

$$\Rightarrow f(\mu+\delta)=1-f(\mu-\delta)$$

8.4

(a)

The accessible states are below.

State number	N	Energy
1	0	0
2	1	ε
3	2	2ε

Thus, the Gibbs sum is

$$Z=\exp(0/\tau)+\exp[(\mu-\varepsilon)/\tau]+\exp[(2\mu-2\varepsilon)/\tau]$$
$$=1+\lambda\exp(-\varepsilon/\tau)+\lambda^2\exp(-2\varepsilon/\tau)$$

The ensemble average occupancy is

$$<N>=\frac{0\times 1+1\times\lambda\exp(-\varepsilon/\tau)+2\times\lambda^2\exp(-2\varepsilon/\tau)}{Z}=\frac{\lambda\exp(-\varepsilon/\tau)+2\lambda^2\exp(-2\varepsilon/\tau)}{Z}$$

(b)

The accessible states are below.

State number	Description	N	Energy
1	(0, 0)	0	0
2	(1, 0)	1	ε
3	(0, 1)	1	ε
4	(1, 1)	2	2ε

Thus, the Gibbs sum is

$$Z=\exp(0/\tau)+\exp[(\mu-\varepsilon)/\tau]+\exp[(\mu-\varepsilon)/\tau]+\exp[(2\mu-2\varepsilon)/\tau]$$
$$=1+2\lambda\exp(-\varepsilon/\tau)+\lambda^2\exp(-2\varepsilon/\tau)$$

The ensemble average occupancy is

$$<N>=\frac{0\times 1+1\times\lambda\exp(-\varepsilon/\tau)+1\times\lambda\exp(-\varepsilon/\tau)+2\times\lambda^2\exp(-2\varepsilon/\tau)}{Z}$$
$$=\frac{2\lambda\exp(-\varepsilon/\tau)+2\lambda^2\exp(-2\varepsilon/\tau)}{Z}$$