Grand canonical ensemble in Hemoglobin (Hb)

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton

(Due date: October 13, 2017)

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company, 1980). p.146 Chapter 5 Problem 6-8.

A red-blooded example of a system that may be occupied by zero molecules or by one molecule is the heme group, which may be vacant or may be occupied by one O_2 molecule – and never any more than one molecule. A single heme group occurs in the protein myoglobin, which is responsible for the red color of meat. If $\varepsilon(O_2)$ is the energy of an adsorbed molecule of O_2 relative to O_2 at rest at infinite distance.

Kittel and Kroemer

5-8. **Carbon monoxide poisoning**. In carbon monoxide poisoning the CO replaces the O_2 adsorbed on hemoglobin (Hb) molecules in the blood. To show the effect, consider a model for which each adsorption site on a heme may be vacant or may be occupied either with energy $\varepsilon(O_2)$ by one molecule O_2 or with energy $\varepsilon(CO)$ by one molecule CO. Let N fixed heme sites be in equilibrium with O_2 and CO in the gas phases at concentrations such that the activities are $z(O_2) = 1 \times 10^{-5}$ and $z(CO) = 1 \times 10^{-7}$, all at body temperature 37°. Neglect any spin multiplicity factors.

(a) First consider the system in the absence of CO. Evaluate $\varepsilon(O_2)$ such that 90 percent of the Hb sites are occupied by O_2. Express the answer in eV per O_2.

(b) Now admit the CO under the specified conditions. Find $\varepsilon(CO)$ such that 10 percent of the Hb sites are occupied by O_2.

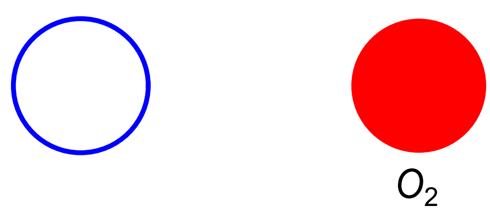


Fig.1 Heme group. Heme site with vacant atom and the state occupied by O_2

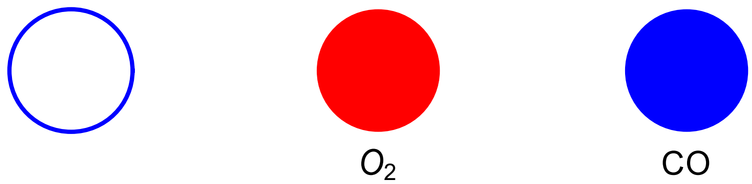
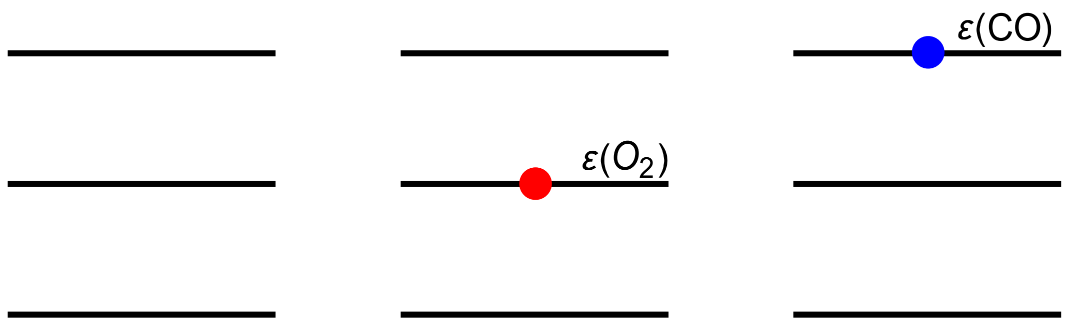


Fig.2 Heme group. Heme site with vacant atom, the state occupied by O_2, and the state occupied by CO. The independent-site model.

((**Solution**))



$N = 0, E = 0$ $\quad$ $N = 1, E = \varepsilon(o_2),\ \mu(o_2)$ $\quad$ $N = 1, E = \varepsilon(\mathrm{Co}),\ \mu(\mathrm{CO})$

First we consider a heme site with vacant atom and the state occupied by O_2. The one-site partition function is

$$Z_G(\mathrm{O_2}) = 1 + z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})},$$

$$P_1(\mathrm{O_2}) = \frac{z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})}}{Z_G(\mathrm{O_2})} = \frac{z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})}}{1 + z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})}}.$$

Next we consider a heme site with three states, a state with vacant atom, a state occupied by O_2, and a state occupied by CO. The grand partition function for the single- site system is given by

$$Z_G(\mathrm{O}, \mathrm{CO}) = 1 + z(\mathrm{O})e^{-\beta\varepsilon(O_2)} + z(\mathrm{CO})e^{-\beta\varepsilon(\mathrm{CO})}.$$

The probability:

$$P_2(\mathrm{O}) = \frac{z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})}}{Z_G(\mathrm{O}, \mathrm{CO})} = \frac{z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})}}{1 + z(\mathrm{O_2})e^{-\beta\varepsilon(O)} + z(\mathrm{CO})e^{-\beta\varepsilon(\mathrm{CO})}},$$

$$P_2(\mathrm{CO}) = \frac{z(CO)e^{-\beta\varepsilon(\mathrm{CO})}}{1 + z(\mathrm{O})e^{-\beta\varepsilon(O_2)} + z(\mathrm{CO})e^{-\beta\varepsilon(\mathrm{CO})}}.$$

((**Example**))

$$P_1(\mathrm{O_2}) = \frac{z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})}}{1 + z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})}} = 0.9$$

$$P_2(\mathrm{O_2}) = \frac{z(\mathrm{O_2})e^{-\beta\varepsilon(\mathrm{O_2})}}{1 + z(\mathrm{O_2})e^{-\beta\varepsilon(O)} + z(\mathrm{CO})e^{-\beta\varepsilon(\mathrm{CO})}} = 0.1$$

where the activity (fugacity)

$$z(\mathrm{O_2}) = 1\times 10^{-5}, \qquad z(\mathrm{CO}) = 1\times 10^{-7}.$$

In other words, the probability of the site being occupied by an oxygen molecule drops from 90% to 10%.

We evaluate the energy of $\varepsilon(\mathrm{O_2})$ and $\varepsilon(\mathrm{CO})$ at T=300 K.

Since

$$z(\mathrm{O_2})e^{-\beta\varepsilon(O_2)}=9 \qquad z(\mathrm{CO})e^{-\beta\varepsilon(CO)}=80,$$

$$e^{-\beta\varepsilon(\mathrm{O_2})} = 9\times 10^5, \qquad e^{-\beta\varepsilon(\mathrm{CO})} = 8\times 10^8$$

we get

$$\varepsilon(\mathrm{O_2}) = -0.35\,\mathrm{eV}, \qquad \varepsilon(\mathrm{CO}) = -0.53\,\mathrm{eV}$$

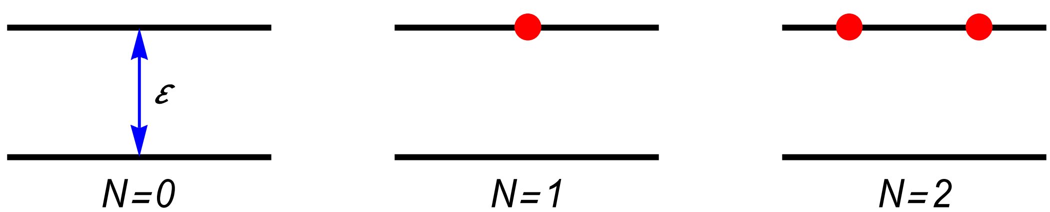
Kittel Thermal Physics
Chapter 6 Problem 3
Distribution function of double occupancy statistics. Let us imagine a new mechanics in which the allowed occupancies of an orbital are 0, 1, and 2. The values of the energy associated with these occupancies are assumed to be 0, ε, and 2ε, respectively.

(a) Derive an expression for the ensemble average occupancy $\langle N \rangle$, when the system composed of this orbital is in thermal and diffusive contact with a reservoir at temperatures T and chemical potential μ.

(b) Return now to the usual quantum mechanics, and derive an expression for the ensemble average occupancy of an energy level which is doubly degenerate; that is, tow orbitals have the identical energy ε. If both orbitals are occupied the total energy 2ε

((**Solution**))

(a)



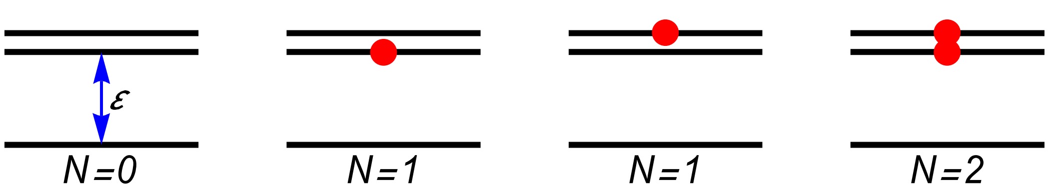
(i) No occupancy, 0 energy ($N = 0$, $E = 0$)
(ii) Single occupancy, ε energy ($N = 1$, $E = \varepsilon$)
(iii) Double occupancy, 2ε energy ($N = 2$, $E = 2\varepsilon$)

Gibbs sum:

$$Z_G = 1 + ze^{-\beta\varepsilon} + z^2 e^{-2\beta\varepsilon}$$

$$\langle N \rangle = z\frac{\partial}{\partial z}\ln Z_G = \frac{ze^{-\beta\varepsilon} + 2z^2 e^{-2\beta\varepsilon}}{1 + ze^{-\beta\varepsilon} + z^2 e^{-2\beta\varepsilon}}$$

(b)



Note that this is a different case than part (a). Now there are a total of 4 states

(i) No occupancy, 0 energy
(ii) Single occupancy, ε energy
(iii) Single occupancy, ε energy

(iv) Double occupancy, 2ε energy

Gibbs sum:

$$Z_G = 1 + ze^{-\beta\varepsilon} + ze^{-\beta\varepsilon} + z^2 e^{-2\beta\varepsilon} = 1 + 2ze^{-\beta\varepsilon} + z^2 e^{-2\beta\varepsilon}$$

$$\begin{aligned}
\langle N \rangle &= z\frac{\partial}{\partial z}\ln Z_G \\
&= \frac{2ze^{-\beta\varepsilon} + 2z^2 e^{-2\beta\varepsilon}}{1 + 2ze^{-\beta\varepsilon} + z^2 e^{-2\beta\varepsilon}} \\
&= \frac{2ze^{-\beta\varepsilon}(1 + ze^{-\beta\varepsilon})}{(1 + ze^{-\beta\varepsilon})^2} \\
&= \frac{2ze^{-\beta\varepsilon}}{1 + ze^{-\beta\varepsilon}}
\end{aligned}$$

REFERENCES

S.J. Blundell and K.M. Blundell, Concepts in Thermal Physics (Oxford, 2006).

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company,1980).