Langmuir adsorption: application of grand canonical ensemble Masatsugu Sei Suzuki Department of Physics, SUNY at Binghamton (Date: August 06, 2023, revised)

Here we discuss the Langmuir adsorption problem using the grand canonical ensemble.

Irving Langmuir (January 31, 1881 – August 16, 1957) was an American chemist and physicist. His most noted publication was the famous 1919 article "The Arrangement of Electrons in Atoms and Molecules" in which, building on Gilbert N. Lewis's cubical atom theory and Walther Kossel's chemical bonding theory, he outlined his "concentric theory of atomic structure". Langmuir became embroiled in a priority dispute with Lewis over this work; Langmuir's presentation skills were largely responsible for the popularization of the theory, although the credit for the theory itself belongs mostly to Lewis. While at General Electric from 1909–1950, Langmuir advanced several basic fields of physics and chemistry, invented the gas-filled incandescent lamp, the hydrogen welding technique, and was awarded the 1932 Nobel Prize in Chemistry for his work in surface chemistry. The Langmuir Laboratory for Atmospheric Research near Socorro, New Mexico, was named in his honor as was the American Chemical Society journal for Surface Science, called Langmuir.

https://en.wikipedia.org/wiki/Irving_Langmuir



Langmuir adsorption as an example of grand canonical ensemble

1. **Method-1** Langmuir adsorption Consider an adsorbent surface having N sites each of which can adsorp one gas molecule. Suppose that it is in contact with an ideal gas with the chemical potential μ . An adsorbed molecule has energy $-\varepsilon_0$ compared to one in a free state. We determine the coverage ratio θ .



Fig. Langmuir adsorption. The number of total sites is N. N_1 sites are occupied by atoms (red, one atom in each site). $(N - N_1)$ sites are not occupied (blue circles). The number of particles is N_1 . The energy of the system is $(-N_1\varepsilon_0)$

When N_1 molecules are adsorbed, the energy is equal to $-N_1\varepsilon_0$. The partition function is evaluated as follows.

$$Z_C(N_1) = \frac{N!}{N_1!(N-N_1)!} \exp(\beta N_1 \varepsilon_0)$$

with N_1 identical molecules. Thus we have

$$Z_{G} = \sum_{N_{1}=0}^{N} z^{N_{1}} Z_{C}(N_{1})$$

= $\sum_{N_{1}=0}^{N} z^{N_{1}} \frac{N!}{N_{1}!(N-N_{1})!} \exp(\beta N_{1}\varepsilon_{0})$
= $\sum_{N_{1}=0}^{N} \frac{N!}{N_{1}!(N-N_{1})!} [z \exp(\beta \varepsilon_{0})]^{N_{1}}$
= $(1 + ze^{\beta \varepsilon_{0}})^{N}$

The average number

$$\begin{split} \left\langle N_{1} \right\rangle &= z \frac{\partial}{\partial z} \ln Z_{G} \\ &= N z \frac{\partial}{\partial z} \ln [1 + z e^{\beta \varepsilon_{0}}] \\ &= N \frac{z e^{\beta \varepsilon_{0}}}{1 + z e^{\beta \varepsilon_{0}}} \end{split}$$

The coverage:

$$\theta = \frac{\langle N_1 \rangle}{N} = \frac{z e^{\beta \varepsilon_0}}{1 + z e^{\beta \varepsilon_0}}$$

In thermal equilibrium,

$$\mu = \mu_{ideal-gas} = k_B T \ln \frac{n}{n_Q},$$

or

$$z = e^{\beta\mu} = \exp[\ln(\frac{n}{n_Q})] = \frac{n}{n_Q} = \frac{P}{k_B T n_Q}$$

where

$$P = nk_BT, \qquad n_Q = \frac{1}{\lambda_{th}^{3}} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = \left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}$$

Then we have the coverage

$$\theta = \frac{\frac{P}{k_B T n_Q} e^{\beta \varepsilon_0}}{1 + \frac{P}{k_B T n_Q} e^{\beta \varepsilon_0}} = \frac{P}{P + P_0(T)}$$

with

$$P_0(T) = k_B T n_Q e^{-\beta \varepsilon_0}$$

We make a plot of $y = P_0(T)\varepsilon_0^{-5/2} (m/2\pi\hbar^2)^{-3/2}$ vs $x = \frac{k_B T}{\varepsilon_0}$



Fig. Plot of the normalized pressure $y = P_0(T)\varepsilon_0^{-5/2} (m/2\pi\hbar^2)^{-3/2}$ vs the normalized temperature $x = \frac{k_B T}{\varepsilon_0}$.

Langmuir's isotherm



Fig. Coverage θ vs the pressure $P/P_0(T)$

2. Method-II: Gibbs sum

This method is much simpler than the above method

For the site 1, there are two states;

(i)	Unoccupied state	
	The number of particles	0
	The energy	0

(ii) Occupied state The number of particles 1 The energy $-\varepsilon_0$

So the partition function is

$$Z_G = 1 + z e^{\beta \varepsilon_0}$$

The probability for an atom in the un-occupied state is

$$P_0 = \frac{1}{Z_G} = \frac{1}{1 + ze^{\beta \varepsilon_0}}$$

The probability for an atom in the occupied state is

$$P_0 = \frac{ze^{\beta\varepsilon_0}}{Z_G} = \frac{ze^{\beta\varepsilon_0}}{1 + ze^{\beta\varepsilon_0}}$$

When the total number of atoms is N, the number of atoms in the occupied state is

$$NP_1 = \frac{Nze^{-\beta\varepsilon_0}}{1+ze^{-\beta\varepsilon_0}}.$$

which is the coverage for the Langmuir isothermal.

2. Experimental results: hydration state in vermiculite



- The octahedral sheet is brucite.
- The basal spacing is from 10 Å to 14 Å.
- It contains exchangeable cations such as Ca²⁺ and Mg²⁺ and two layers of water within interlayers.
- It can be an excellent insulation material after dehydrated.

Here are our experimental results in Na vermiculite and Ca-vermiculite. These experiments were done at the Schlumbeger-Doll Research in Connecticut in 1986 with Dr. M. Stanley Whittingham (currently, Professor of the Chemistry in Binghamton University, getting a Nobel prize in chemistry, 2019, on lithium-ion battery, alongside Akira Yoshino and John B. Goodenough). We measure the weight of the system when water molecules are intercalated in the inter-lamellar space of vermiculite (a sort of clay having layered structures). The system is exposed to the water vapor pressure. When the water vapor pressure is changed at a constant temperature, the water molecules are intercalated into the inter-lamellar space. There are two states, one-water layer state (one water layer in the same inter-lamellar space), and two water-later state (two water layers in the same inter-lamellar space). Our experimental results are shown as follows.



Fig. Water hydration states in Na-vermuculite. There are two states depending on the water vapor pressure. n is the weight ratio of water vs Na-vermiculite.



FIG. 5. Water-adsorption isotherm for Ca vermiculite at various temperatures. •, $T=297 \ K$; \triangle , 299 K; \blacktriangle , 310 K; \bigcirc , 318 K; \blacktriangledown , 358 K; \times , 371 K.

Fig. Water-adsorption isotherm for Ca vermiculite at various fixed temperatures. The phase transition occurs in two steps; zero hydration state, one water layer state, and two water layer state.

M. Suzuki, N. Wada, D.R. Hines, and M.S. Whittingham, Phys. Rev. B 36, 2844 (1987) Hydration states and phase transitions in vermiculite intercalation compounds.

3. Method-2

The form of Z_{G} indicates that the adsorption of atom is independent of sites.

 $Z_G = Z(1)Z(2)...Z(N)$

where Z(i) is the on-site partition function for the site i. Since the sites are homogeneously,

$$Z(1) = Z(2) = \dots = Z(N)$$

Then we have

$$Z_G = [Z(1)]^N$$

For the site 1, there are two states;

The number of particles	0
The energy	0
The number of particles	1
The energy	$-\mathcal{E}_0$

So that the partition function for the site 1 is given by

$$Z(1) = 1 + z e^{\beta \varepsilon_0}$$

The Grand partition function for the N site system is

$$Z_G = (1 + z e^{\beta \varepsilon_0})^N$$

Probability of finding the particle in the $|0\rangle$

$$P(|0\rangle) = \frac{1 Z(2)...Z(N)}{Z(1)Z(2)...Z(N)} = \frac{1}{Z(1)} = \frac{1}{1 + ze^{\beta \varepsilon_0}}$$

Probability of finding the particle in the $\left|1\right\rangle$

$$P(|1\rangle) = \frac{ze^{\beta\varepsilon_0} \ Z(2)...Z(N)}{Z(1)Z(2)...Z(N)} = \frac{ze^{\beta\varepsilon_0}}{Z(1)} = \frac{ze^{\beta\varepsilon_0}}{1+ze^{\beta\varepsilon_0}}$$

4. Method-3

We calculate the partition function in a numerical way.

$$Z_{G} = \sum_{ASN} \exp[\beta(\mu N - E)]$$

$$N = n_{1} + n_{2} + n_{3} + \dots + n_{N}$$

$$E = -\varepsilon_{0}(n_{1} + n_{2} + n_{3} + \dots + n_{N})$$

$$Z_{G} = \left(\sum_{n_{1}} \exp[\beta(\mu + \varepsilon_{0})n_{1}\right) \left(\sum_{n_{2}} \exp[\beta(\mu + \varepsilon_{0})n_{2}\right) \dots \left(\sum_{n_{N}} \exp[\beta(\mu + \varepsilon_{0})n_{N}\right)$$

$$= \left(\sum_{n_{1}} \exp[\beta(\mu + \varepsilon_{0})n_{1}\right)^{N}$$

$$= (1 + ze^{\beta\varepsilon_{0}})^{N}$$

Probability for finding a particle in the $\left|0\right\rangle$ state.

$$P(|0\rangle) = \frac{1\left(1 + ze^{\beta\varepsilon_0}\right)^{N-1}}{\left(1 + ze^{\beta\varepsilon_0}\right)^N} = \frac{1}{1 + ze^{\beta\varepsilon_0}}$$

or

$$\langle n_0 \rangle = 1P_0 + 0P_1 = \frac{1}{1 + ze^{\beta \varepsilon_0}}$$

Probability for finding a particle in the 1 state.

$$P(|1\rangle) = \frac{\lambda e^{\beta \varepsilon_0} (1 + z e^{\beta \varepsilon_0})^{N-1}}{(1 + z e^{\beta \varepsilon_0})^N} = \frac{z e^{\beta \varepsilon_0}}{1 + z e^{\beta \varepsilon_0}}$$

$$\langle n_1 \rangle = 0 P_0 + 1 P_1 = \frac{z e^{\beta \varepsilon_0}}{1 + z e^{\beta \varepsilon_0}}$$

What does this mean? Is this one-particle problem? \rightarrow The answer is yes.

$$Z_1 = \sum_{n_1} \exp[\beta(\mu + \varepsilon_0)n_1] = 1 + ze^{\beta\varepsilon_0}$$

The coverage is derived as

$$f = z \frac{\partial}{\partial z} \ln Z_1$$

$$= z \frac{\partial}{\partial z} \ln[1 + ze^{\beta \varepsilon_0}]$$

$$= \frac{ze^{\beta \varepsilon_0}}{1 + ze^{\beta \varepsilon_0}}$$

$$Z_G(\beta, \mu) = \sum_{N_1=0}^N \frac{N!}{N_1!(N - N_1)!} z^{N_1} e^{-N_1\beta(-\varepsilon_0)}$$

$$= \sum_{N_1=0}^N \frac{N!}{N_1!(N - N_1)!} (ze^{\beta \varepsilon_0})^{N_1}$$

$$= (1 + ze^{\beta \varepsilon_0})^N$$

$$= Z_1^N$$

where Z_1 is the partition function for the site 1,

$$Z_1 = \sum_{N=0}^{1} \sum_{i[N]} z^N \exp[-\beta E_i(N)] = 1 + z e^{-\beta(-\varepsilon_0)} = 1 + z e^{\beta\varepsilon_0}.$$

((Note))

or



In the site 1, there are two states;

$$N = 0 0 energy N = 1, -\varepsilon_0$$

The partition function is

$$Z_{C1} = 1 + z e^{-(-\beta \varepsilon_0)}$$

5. Number fluctuation

$$\left\langle N_1^2 \right\rangle - \left\langle N_1 \right\rangle^2 = z \frac{\partial}{\partial z} z \frac{\partial}{\partial z} \ln Z_G$$
$$= N^2 \frac{z e^{\beta \varepsilon_0}}{\left(1 + z e^{\beta \varepsilon_0}\right)^2}$$

This result can be obtained using the concept of probability.

$$P = \frac{ze^{\beta \varepsilon_0}}{1 + ze^{\beta \varepsilon_0}}$$
 for finding one atom occupied at the specific site.
$$Q = 1 - P = \frac{1}{1 + ze^{\beta \varepsilon_0}}$$
 for finding no atom at the specific site.

We note that

$$\langle N_1 \rangle = NP = N \frac{z e^{\beta \varepsilon_0}}{1 + z e^{\beta \varepsilon_0}}$$

$$\left\langle N_{1}^{2}\right\rangle = N^{2}P = N^{2}\frac{ze^{\beta\varepsilon_{0}}}{1 + ze^{\beta\varepsilon_{0}}}$$

The number fluctuation:

$$\langle N_1^2 \rangle - \langle N_1 \rangle^2 = N^2 P - N^2 P^2 = N^2 P (1 - P) = N^2 P Q = \frac{N^2 z e^{\beta \varepsilon_0}}{\left(1 + z e^{\beta \varepsilon_0}\right)^2}$$

or

$$\frac{\left\langle N_{1}^{2}\right\rangle - \left\langle N_{1}\right\rangle^{2}}{N^{2}} = \frac{ze^{\beta\varepsilon_{0}}}{\left(1 + ze^{\beta\varepsilon_{0}}\right)^{2}}$$

REFERENCES

J.G. Dash, Films on Solid Surfaces The Physics and Chemistry of Physical Adsorption (Academic Press, 1975).

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

APPENDIX

Problem 5-6,

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

6. Gibbs sum for a two level system.

(a) Consider a system that may be unoccupied with energy zero or occupied by one particle in either of two states, one of energy zero and one of energy ε . Show that the Gibbs sum for this system is

$$Z_1 = 1 + z + ze^{-\beta\varepsilon}$$

Our assumption excludes the possibility of one particle in each state at the same time. Notice that we include in the sum a term for N = 0 as a particular state of a system of a variable number of particles.

(b) Show that the thermal average occupancy of the system is

$$\langle N \rangle = \frac{z + z e^{-\beta \varepsilon}}{Z_1}.$$

(c) Show that the thermal average occupancy of the state at energy ε is

$$\langle N(\varepsilon) \rangle = \frac{z e^{-\beta \varepsilon}}{Z_1}.$$

- (d) Find an expression for the thermal average energy of the system.
- (e) Allow the possibility that the orbital at 0 and at ε may be occupied each by one particle at the same time; show that

$$Z_1 = 1 + z + ze^{-\beta\varepsilon} + z^2 e^{-\beta\varepsilon} = (1+z)(1+ze^{-\beta\varepsilon})$$

Because Z_1 can be factored as shown, we have in effect two independent systems.

((Solution))

(a - (d)

We consider a system where



The probability for each state is given by

$$P_1 = \frac{1}{Z_1}, \qquad P_2 = \frac{z}{Z_1}, \qquad P_3 = \frac{ze^{-\beta\varepsilon}}{Z_1}$$

where

$$Z_1 = 1 + z + z e^{-\beta \varepsilon}$$

The average number:

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln Z_G \qquad \langle N \rangle = 0P_1 + 1P_2 + 1P_3 = \frac{1}{Z_1} (z + ze^{-\beta\varepsilon}) \qquad = \frac{1}{Z_1} (z + ze^{-\beta\varepsilon})$$

The thermal average occupancy of the state at the energy ε .

$$1 P_3 = \frac{1}{Z_1} z e^{-\beta \varepsilon}$$

The thermal average energy of the system

$$\langle E \rangle = 0P_1 + 0P_2 + \varepsilon P_3$$

= $\frac{1}{Z_1} \varepsilon (ze^{-\beta \varepsilon})$

(d)



For each site, there are four states. vacant state (no atom)

one atom at the energy 0 level

one atom at the energy ε level

One atom at the energy 0 level and the other atom at the energy ε level.

The Gibbs sum is

$$Z_1 = 1 + z + ze^{-\beta\varepsilon} + z^2 e^{-\beta\varepsilon} = (1+z)(1+ze^{-\beta\varepsilon})$$

Because Z_G can be factored as shown, we have in effect two independent systems.