Adsorption

The Langmuir Adsorption Curve (*1*)

Adsorption phenomena take place between a fluid (which might be a liquid or a gas) and a surface. The surface can either mean one surface of a solid, which should then be treated as a two-dimensional problem (the fluid will not interact with the bulk of the solid), or it can also be the interaction with a very long and "linear" molecule (like a polymer), for which we should treat the surface as being one-dimensional. It is furthermore possible to establish a non-planar surface, which just brings a more complicated formalism when it comes to interaction sites. For simplicity, we will call this one- or two-dimensional surface where adsorption takes place as the lattice (as an alternative to the adsorbent).

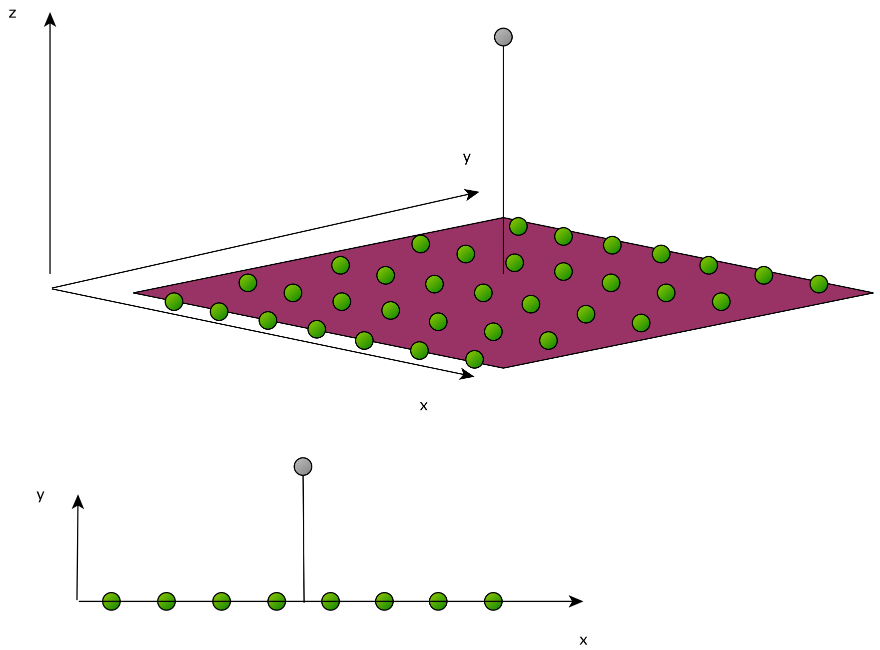

Figure 1: Interaction of a gas molecule with a two- and a one-dimensional surface.

When treating adsorption problems, one assumes that the interactions between the small molecule and the surface are weak, mostly of van der Waals type. This means that the forces keeping the lattice together are so strong that they are unaffected by the adsorption equilibrium phenomenon. The lattice works then as a field for the adsorbate (the molecules of a gas or liquid adhering to the surface of the adsorbent). On the other hand, the same applies for adsorbate molecules, *i.e.* the forces keeping these molecules together are strong enough to be unperturbed by the lattice. When adsorbate and adsorbent interact, the free translation of the adsorbate along the direction orthogonal to the lattice is transformed into a van der Waals interaction, which can be approximated by a Lennard-Jones potential,

$$U(x = const, y = const, z) = \frac{a}{z^{12}} - \frac{b}{z^6} \tag{1}$$

where a and b are constants (which are related in a truly Lennard-Jones potential). Due to the lattice nature of the adsorbent, the potential U should also be a function of x and eventually y. This part of the potential is however periodic with maxima on the positions of atoms on the adsorbent's lattice, meaning that the x and y dependencies of U are described by some oscillatory function. For simplicity, lets assume that the lattice has a particle located in the origin of the referential, meaning that the x and y dependencies are simply given by cosine functions.

$$\begin{aligned} U(x, y = const, z = const) &= V_{0x} cos(cx) \\ U(x = const, y, z = const) &= V_{0y} cos(dy) \end{aligned} \tag{2}$$

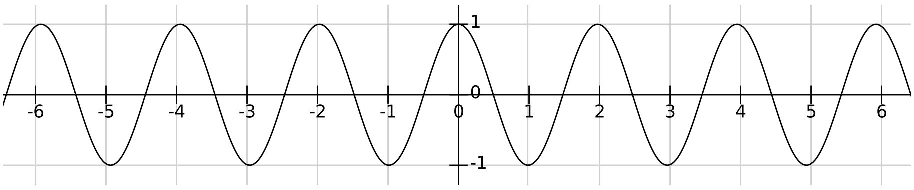

Figure 2: Generic plot for the interaction potential between adsorbate and adsorbent along the x direction for $V_0 = 1$. Plot generated using fooplot (*2*).

Because of the arising interaction, translation of adsorbate is no longer free and the statistical mechanical treatment of the translation degrees of freedom of the adsorbate is to be replaced by a vibrational type of interaction. Since we assumed that the inner forces of the adsorbate are unaffected, the general single-particle partition function for the system becomes

$$Q(T) = q_{1D}^{trans} q^y q^z e^{-\frac{U_0}{k_B T}} q^{rot} q^{vib} q^{el} \tag{3}$$

for a one-dimensional lattice (for which there is still one free translational degree of freedom) or, for a two-dimensional lattice,

$$Q(T) = q^x q^y q^z e^{-\frac{U_0}{k_B T}} q^{rot} q^{vib} q^{el} \tag{4}$$

The partition functions q^{vib} and q^{el} contain terms from both adsorbate and adsorbent. This includes not only the electronic structure but also vibrational terms for both systems. The rotational term (q^{rot}) concerns solely the adsorbate but it also contains indirectly the influence of the adsorbent because the interaction adsorbent-adsorbate affects slightly the bond lengths of adsorbate. This term is therefore different from the free-adsorbate rotational partition function such that in some extreme cases it might even be replaced by a vibrational-like partition function.

The partition functions above defined describe the system of a single adsorbate getting adsorbed on a surface. In a real chemical system there are however many adsorbate molecules. This approximation is valid under the ideal gas approximation and the partition function for the complex system of N adsorbate molecules adsorbing on a surface can be obtained by distributing the N adsorbate particles over M binding/adsorbing sites. Assuming that all particles are indistinguishable and that each binding site can only take up to one adsorbate molecule, the total partition function is simply given by

$$Z(T) = \frac{M!(Q(T))^N}{N!(M-N)!} \tag{5}$$

To describe the system of a free gas in equilibrium with adsorbed gas on the lattice one requires the chemical potential. By definition we may write

$$\frac{\mu}{k_BT} = -\left(\frac{\partial logZ(T)}{\partial N}\right)_{M,T} \tag{6}$$

and by making use of the Stirling approximation for logarithms

$$\frac{\mu}{k_BT} = -(-logN + log(M-N) + logQ) = log\left(\frac{N}{Q(M-N)}\right) = log\left(\frac{\theta}{Q(1-\theta)}\right) \tag{7}$$

where $\theta = \frac{N}{M}$ is the fraction of adsorption sites occupied. If we now invoke the equilibrium condition, then

$$\frac{\mu^{ads}}{k_BT} = log\left(\frac{\theta}{Q(1-\theta)}\right) = \frac{\mu^{gas}+\mu^{lat}}{k_BT} = \frac{\mu^{0,gas}}{k_BT} + logP + \frac{\mu^{lat}}{k_BT} \tag{8}$$

where $\mu^{0,gas}$ is the chemical potential of the gas at standard conditions and μ^{lat} is the chemical potential for the free surface (without any adsorbed molecule). Rearranging this expression yields,

$$e^{\frac{\mu^{0,gas}+\mu^{lat}}{k_BT}} = \lambda = \frac{\theta}{PQ(1-\theta)} \Leftrightarrow Q\lambda = \chi = \frac{\theta}{P(1-\theta)} \Leftrightarrow \theta = \frac{\chi P}{1+\chi P} \tag{9}$$

which is the expression for Langmuir's adsorption isotherm.

It is also instructive to obtain the system's entropy using the definition:

$$\begin{aligned} S &= k_B T\frac{\partial logZ}{\partial T} + k_B logZ = Nk_B T\frac{\partial logQ}{\partial T} + k_B log\frac{M!Q^N}{N!(M-N)!} \\ &= k_B log\frac{M!}{N!(M-N)!} + Nk_B\left(logQ + T\frac{\partial logQ}{\partial T}\right) = S_{config} + S_{vib} \end{aligned} \tag{10}$$

We can therefore see that the entropy for the system has two main components, one vibrational in nature, and the other configurational in nature that describes all the possible ways the adsorbate molecules distribute themselves over the adsorbent. Other thermodynamic functions follow similarly from their respective definition.

First principle estimation of adsorption isotherms

Re-deriving the Langmuir equation based on statistical mechanical grounds adds the value of connecting the Langmuir constant χ with mechanical force parameters (or in reality with parameters describing the potential energy between adsorbate and adsorbent). This opens doors to direct calculation of adsorption isotherms using first principle methods. Such calculation requires the use of electronic structure methods that are able to accurately describe both the lattice and the adsorbate together, for which in general Density Functional Theory (DFT) or Density Functional Tight Binding (DFTB) methods should be preferred. The inclusion of long-range dispersion terms and non-covalent interactions is going to be crucial, for which we definitely advise the use of the dispersion corrected methods of Grimme (*3–5*). For accurate enough calculations one shall require relatively large/extended systems, which will render the simulations anyway cumbersome. It requires also that one knows microscopically how the lattice looks like so that practical calculations can be undertaken, which might be a problem for many if not most cases. If there is no structure for the adsorbent known, then DFTB might be used in some cases to determine the most probable adsorbent structure that exists. This assumes or demands that the adsorbent has some sort of periodicity in its structure. After optimizing geometries for the interaction adsorbent-adsorbate one requires a vibrational frequency calculation to describe the potential surface around the minimum. With this information one has then everything to calculate χ. By definition

$$\chi = Q_{ads} e^{\frac{\mu^{0,ig} + \mu^{lat}}{k_B T}} \tag{11}$$

The chemical potentials for the isolated adsorbate and adsorbent can be obtained using the standard models described in another PDF (particle-in-a-box, rigid rotor, harmonic oscillator and the electronic partition function at the basic level; any other more evolved method would also be applicable). The other quantity we need is Q_{ads}, which contains the minimum energy for the potential interaction adsorbate-adsorbent ($e^{-\frac{U_0}{k_B T}}$; this quantity can be directly obtained by simulation), the respective vibrational frequencies (in x, y and z that would give q^x, q^y, q^z) and the partition functions for the adsorbate adsorbed to the adsorbent (q^{rot}, q^{vib}, q^{el}). Note that in the latter the contributions from the adsorbent might be approximately the same as in the case of an isolated lattice, which then cancels with the terms coming from the chemical potential for the free adsorbent. The same simplification should however never take place for the adsorbate.

Finally, all terms q^x, q^y, q^z are vibrational in nature (replacing the 3 directions of translation for the free particle). One could in principle use the harmonic oscillator approximation, however, since we speak usually of very subtle/weak interactions, this model is doomed to fail because it cannot possibly account for probably high degree of anharmonicity of the potential. One should at least expect high deviations to experimental data stemming from this contribution. At lower temperatures the respective entropic terms are furthermore expected to explode. One should then use more refined models for this partition function that can account for such effects.

Alternatively (*6*), we may use a "thermodynamic definition" of χ, by expressing χ as a function of the adsorption Gibbs free energy. In order to get that relation we rewrite the chemical potential terms explicitly as functions of partition functions to get

$$\chi = \frac{Q_{MS}}{Q_M Q_S} \tag{12}$$

where M is the adsorbate, S the adsorbent and MS (or alternatively $M\cdots\cdots\cdots S$ to make explicit the non-covalent nature of the interaction) is the bound pair. Since in our definitions the partition functions are complete (*i.e.* they contain zero point vibrational energies), then we can compare χ to an equilibrium constant (*7*) for the informal addition reaction

$$M + S = M\cdots\cdots\cdots S \tag{13}$$

In this case it results that

$$\chi = exp\left(-\frac{\Delta_{ads}G}{k_B T}\right) = exp\left(\frac{\Delta_{ads}S}{k_B}\right) exp\left(-\frac{\Delta_{ads}H}{k_B T}\right) \tag{14}$$

where $\Delta_{ads}G$, $\Delta_{ads}S$ and $\Delta_{ads}H$ are the thermodynamic descriptors for the reaction above specified.

The model above considers however a single binding site available in the surface. It is also possible to consider several binding sites with the multi-Langmuir model:

$$\chi = \sum\nolimits_{i}^{sites} \frac{\chi_i P}{1+\chi_i P} \tag{15}$$

This might however become a problem for the quantum chemical method because it requires one to explicitly think of all possible interactions between adsorbent and adsorbate. While that is certainly possible and doable for small adsorbate molecules and relatively flat adsorbents, it only requires a larger adsorbate or a porous solid (like a silicate) for the direct quantum chemical approach to become extremely cumbersome and impracticable. In that case one has to resort to either Monte Carlo or molecular dynamics and let the system visit virtually all the stable interactions/configurations available to its potential energy surface. One successful example of the Monte Carlo method applied to adsorption problems is for instance here (*8*). Both these techniques allow furthermore to introduce some dynamical aspects to the simulation (for instance the Monte Carlo technique suffers also from diffusion problems for larger adsorbates in the pores of the adsorbent) and they allow for the matrix defining the adsorbent to be not fixed.

Furthermore, the adsorption isotherms calculated above take by no means in consideration possible interactions between neighbouring adsorbed molecules. These interactions may however be approximately included using the adsorption reaction for multiple adsorbates

$$nM + S = M_n \cdots\cdots\cdots S \tag{16}$$

Note that due to the inherent difficulty in representing schematically the adsorption process, the equation above implies that different M molecules are bound to different active sites, as it is required by the basic Langmuir isotherm. Electronic energies can then be renormalized for single molecule using

$$\Delta_{ads} E = \frac{E_{M_n S} - E_S - nE_M}{n} \tag{17}$$

where the subscripts in energy indicate the specific isolated system. This approach considers interactions between neighbouring particles as a completely static effect (which would still be somehow consistent with Langmuir adsorption.

More realistic systems require however inclusion of interactions between neighbouring adsorbed particles. The Bragg-Williams mean-field approximation is one possibility (that we will not explore further in this text) that may be used to estimate the adsorption isotherm constant χ (*6, 9*). This approach can be used to improve results on multilayer adsorption systems as well and requires a dynamic simulation of the system (either molecular dynamics or monte carlo). This can however be to some good extent solved in static quantum chemical simulations by taking a "self-consistency" approach, because the total energy of neighbours is dependent on the coverage of the adsorbent surface. In this self-consistent approach one starts by determining the surface coverage for the system without neighbour interactions and from there we estimate the total energy arising from neighbour interactions. This is then used to estimate a new surface coverage, and so on. Alternative procedures based solely on the statistical mechanics of the systems are explored in more detail below. Note however these solutions might not be valid for two- or three-dimensional systems. In that case other techniques in statistical mechanics must be employed.

Free Particle over Surface (*1*)

If the interaction between adsorbate and adsorbent is weak enough, it is possible for the adsorbate molecule to be mobile over the lattice. In this case, the z interaction of the potential remains the same. However, the x and y components of the adsorbate-adsorbent interaction vanishes and a particle in a D-dimensional box ($D = 1, 2$) becomes the adequate model for describing the adsorbate on the lattice. In this case we use

$$q^x q^y = \left(\frac{2\pi m k_B T}{h^2}\right) A \tag{18}$$

where m is the adsorbate's mass and A the adsorbent's surface area, which we here assumed to be two-dimensional. Since the adsorbate moves over the lattice, the configurational term vanishes to $(N!)^{-1}$ as now we must only take into account the fact that adsorbate molecules are indistinguishable also on top of the surface. The total partition function for the adsorption system becomes

$$Z(T) = \frac{(Q(T))^N}{N!} \tag{19}$$

with the single-particle partition function given by

$$Q(T) = \left(\frac{2\pi m k_B T}{h^2}\right) A q^z e^{-\frac{U_0}{k_B T}} q^{rot} q^{vib} q^{el} \tag{20}$$

The chemical potential reads then

$$\frac{\mu}{k_B T} = -\left(\frac{\partial log Z(T)}{\partial N}\right)_{A,T} = -\frac{\partial}{\partial N}\left(N log Q - log N!\right) = log\left(\frac{N}{Q}\right) \tag{21}$$

The adsorption isotherm can be obtained similarly to the previous case, by demanding the equality of chemical potentials:

$$\begin{aligned} \frac{\mu^{ads}}{k_BT} = log\left(\frac{N}{Q}\right) = \frac{\mu^{gas}+\mu^{lat}}{k_BT} = \frac{\mu^{0,gas}+\mu^{lat}}{k_BT} + logP \Leftrightarrow Pe^{\frac{\mu^{0,gas}+\mu^{lat}}{k_BT}} = \frac{N}{Q} \\ \Leftrightarrow \frac{N}{A} = \bar{\theta} = \frac{2\pi m k_BT}{h^2} q^z e^{-\frac{U_0}{k_BT}} e^{\frac{\mu^{0,gas}+\mu^{lat}}{k_BT}} P = \bar{\chi}P \end{aligned} \tag{22}$$

Combining this model with the Langmuir partition function it is possible to estimate the ratio between mobile and fixed (localized) molecules over the surface

$$\frac{N_{mobile}}{N_{local}} = \frac{Q_{mobile}}{MQ_{local}} = \frac{2\pi m k_BTA}{q^xq^yh^2M} \tag{23}$$

Note that since the partition function for the localized adsorbate molecules refers only to a single binding site instead of the whole adsorbent lattice, one has to multiply this partition function by the total number of binding sites to make the comparison even.

Introducing Adsorbate Interactions (*1*)

In this section we consider a linear (one-dimensional) adsorbing system without any boundary effects, *i.e.*, with $M \to +\infty$. Each binding site can be at most occupied by a single molecule, performing a total number of N occupied sites. If adsorbate molecules have no interaction, the solution was already discussed and one obtains the Langmuir isotherm. In this section however, we assume that adsorbate molecules can interact with their nearest neighbours on the linear surface. The interaction energy is furthermore assumed to be ω. In this situation we must consider several types of occupations: binding sites consecutively occupied (N_{11} in total); alternatively occupied binding sites (N_{01} in total); consecutively empty sites (N_{00} in total). Since each 11 configuration takes two molecules, one obtains a total of $2N = 2N_{11} + N_{01}$ occupied sites and a total of $M = N_{00} + N_{01} + N_{11}$ binding sites. Since there are three variables for two equations, one of the variables has to be left independent. We will choose N_{01} to be such variable. The total potential (interaction) energy in a system with N_{01} singly occupied pairs of sites is given by

$$N_{11}\omega = \left(N - \frac{N_{01}}{2}\right)\omega \tag{24}$$

Furthermore, we will define $g(N, M, N_{01})$ as the number of possible ways to distribute N particles over $M \leq N$ sites, which leads to N_{01} singly occupied sites. The canonical partition function is then in this case

$$\begin{aligned} Z(N,M,T) = Q^N {\textstyle\sum_{N_{01}}} g(N,M,N_{01}) exp\Big(- \left[N - \frac{N_{01}}{2} \right] \frac{\omega}{k_B T} \Big) \\ = \Big(Qe^{-\frac{\omega}{k_B T}} \Big)^N {\textstyle\sum_{N_{01}}} g(N,M,N_{01}) e^{\frac{\omega N_{01}}{2 k_B T}} \end{aligned} \tag{25}$$

From the first section we know that in the limiting case $\omega = 0$

$$ {\textstyle\sum_{N_{01}}} g(N,M,N_{01}) = \frac{M!}{N!(M-N)!} \tag{26}$$

To determine g in the general case we must distribute N_{11} pairs over N occupied positions and N_{00} pairs over $M-N$ vacant positions, given the conditions previously determined. Using the respective combinations and multiplying them we obtain

$$ g(N,M,N_{01}) = \frac{N!(M-N)!}{(\frac{N_{01}}{2})!(N - \frac{N_{01}}{2})!(\frac{N_{01}}{2})!(M - N - \frac{N_{01}}{2})!} \tag{27}$$

Insertion into the partition function yields

$$ Z(N,M,T) = \Big(Qe^{-\frac{\omega}{k_B T}} \Big)^N {\textstyle\sum_{N_{01}}} \frac{N!(M-N)! e^{\frac{\omega N_{01}}{2 k_B T}}}{(\frac{N_{01}}{2})!(N - \frac{N_{01}}{2})!(\frac{N_{01}}{2})!(M - N - \frac{N_{01}}{2})!} \tag{28}$$

Performing the sum in equation 28 over all possible values for N_{01} is extremely difficult, if not impossible. However, it is to expect that in problems like this a single value of N_{01} has the largest contribution and that all other terms are negligible. To find that maximum we must find the maximum of the term being summed or its logarithm. For that we require the first derivative to be zero. Getting then the first derivative of the logarithm of the combinatorial term yields

$$\begin{aligned} \frac{\partial}{\partial N_{01}} \left[log N! + log(M-N)! + \frac{N_{01}\omega}{2 k_B T} \right] \\ \frac{\partial}{\partial N_{01}} \left[-2 log \left(\frac{N_{01}}{2} \right)! - log \left(N - \frac{N_{01}}{2} \right)! - log \left(M - N - \frac{N_{01}}{2} \right)! \right] \\ = \frac{\partial}{\partial N_{01}} \left[\frac{N_{01}\omega}{2 k_B T} - 2 log \left(\frac{N_{01}}{2} \right)! - log \left(N - \frac{N_{01}}{2} \right)! - log \left(M - N - \frac{N_{01}}{2} \right)! \right] \\ = \frac{\omega}{2 k_B T} - log \frac{N_{01}}{2} + \frac{1}{2} log \left(N - \frac{N_{01}}{2} \right) + \frac{1}{2} log \left(M - N - \frac{N_{01}}{2} \right) \end{aligned} \tag{29}$$

By zeroing the result above and by replacing the values for N_{00} and N_{11} we obtain the condition

$$ \frac{N_{00} N_{11}}{N_{01}^2} = \frac{1}{4} e^{-\frac{\omega}{k_B T}} \tag{30}$$

Note that this condition is equivalent to the chemical equilibrium for the reaction

$$2N_{01} \leftrightharpoons N_{00} + N_{11} \tag{31}$$

with equilibrium constant $\frac{1}{4}e^{-\frac{\omega}{k_B T}}$. Since N_{00} and N_{11} are dependent variables, we go back to express them in terms of N_{01} and we obtain the equation

$$NM - N^2 - M\frac{N_{01}}{2} + \frac{N_{01}^2}{4}\left(1 - e^{-\frac{\omega}{k_B T}}\right) = 0 \tag{32}$$

This is a quadratic function in N_{01} which has solutions

$$\begin{aligned} N_{01} &= \frac{M \pm \sqrt{M^2 - 4(NM - N^2)\left(1 - e^{-\frac{\omega}{k_B T}}\right)}}{1 - e^{-\frac{\omega}{k_B T}}} \\ = M &\left(\frac{1 \pm \sqrt{1 - 4(\theta - \theta^2)\left(1 - e^{-\frac{\omega}{k_B T}}\right)}}{1 - e^{-\frac{\omega}{k_B T}}}\right) = M\left(\frac{1 \pm \beta}{1 - e^{-\frac{\omega}{k_B T}}}\right) \end{aligned} \tag{33}$$

Note that if the square root term is not complex then one has two real solutions to the equation. Of the two roots, the "minus" one consists of a system with almost all binding sites consecutively occupied or consecutively vacant (since regions of consecutive occupation and consecutive vacancy are highly improbable). We therefore choose the "plus" root which also should correspond to milder interaction ω between adsorbate molecules. Using this value in the partition function one gets

$$Z(N, M, T) = \left(Qe^{-\frac{\omega}{k_B T}}\right)^N \frac{N!(M-N)!e^{\frac{\omega N_{01}}{2k_B T}}}{(\frac{N_{01}}{2})!(N - \frac{N_{01}}{2})!(\frac{N_{01}}{2})!(M - N - \frac{N_{01}}{2})!} \tag{34}$$

This allows us to determine thermodynamic properties for our system. Of particular interest is again the chemical potential. Since N_{01} is an independent variable,

$$\begin{aligned} \mu = -k_B T\left(\frac{\partial log Z}{\partial N}\right)_{M,T} &= -k_B T log\left(Qe^{-\frac{\omega}{k_B T}}\right) - k_B T log\frac{N\left(M - N - \frac{N_{01}}{2}\right)}{(M - N)\left(N - \frac{N_{01}}{2}\right)} \\ &= -k_B T log\left(Qe^{-\frac{\omega}{k_B T}}\right) - k_B T log\frac{\theta\left(1 - \theta - \frac{N_{01}}{2M}\right)}{(1 - \theta)\left(\theta - \frac{N_{01}}{2M}\right)} \end{aligned} \tag{35}$$

If we set $\alpha = \frac{N_{01}}{2M}$ this results in

$$\mu = -k_B T log\left(Qe^{-\frac{\omega}{k_B T}}\right) - k_B T log\frac{\theta(1 - \theta - \alpha)}{(1 - \theta)(\theta - \alpha)} \tag{36}$$

Comparing now the chemical potential of the adsorbed gas with the gaseous phase with the free surface we can determine the adsorption isotherm.

$$\frac{\mu^{ads}}{k_BT} = \frac{\mu^{0,gas} + \mu^{lat}}{k_BT} + logP = -log\left(Qe^{-\frac{\omega}{k_BT}}\right) - log\frac{\theta\left(1-\theta-\alpha\right)}{\left(1-\theta\right)\left(\theta-\alpha\right)} \tag{37}$$

In the way they are formulated, the equations depend on α. A better formulation however, makes use the parameter β instead. This is because we can easier see the effects of removing the interaction between bound adsorbates to form the Langmuir curve (in the Langmuir case $\beta = 1$ and $\omega = 0$). Reformulating the last equation in terms of β we obtain after some algebra

$$P\chi e^{-\frac{\omega}{k_BT}} = \frac{(1-\theta)(\beta-1+2\theta)}{1+\beta-3\theta-\theta\beta+2\theta^2} \tag{38}$$

for which two possible ways of solving the equation are possible. On one hand, the β dependency on θ can be momentarily ignored and we solve the above equation for θ. This results in

$$\theta = \frac{P\chi e^{-\frac{\omega}{k_BT}}(3+\beta)+3-\beta-\sqrt{P^2\chi^2e^{-\frac{2\omega}{k_BT}}(1-\beta)^2+1+\beta^2+2P\chi e^{-\frac{\omega}{k_BT}}(1-\beta^2)}}{4\left(1+P\chi e^{-\frac{\omega}{k_BT}}\right)} \tag{39}$$

where we neglected the positive term from the resolvent formula because it is not in agreement with the limiting case of the Langmuir isotherm. To solve this equation we make a starting guess for β, we calculate θ and update β respectively until self-consistency is reached.

Alternatively, we can isolate β from equation 38 and solve the resulting quartic polynomial. If we isolate β we obtain

$$\beta = \left(\frac{1+P\chi e^{-\frac{\omega}{k_BT}}}{1-P\chi e^{-\frac{\omega}{k_BT}}}\right)\frac{2\theta^2-3\theta+1}{1-\theta} \tag{40}$$

which yields

$$\begin{aligned}4\theta^4\left(1-e^{-\frac{\omega}{k_BT}}-z\right)-12\theta^3\left(1-e^{-\frac{\omega}{k_BT}}-z\right)+\theta^2\left(13-12e^{-\frac{\omega}{k_BT}}-13z\right)\\ -\theta\left(6-4e^{-\frac{\omega}{k_BT}}-6z\right)+1-z=0\end{aligned} \tag{41}$$

where

$$z = \left(\frac{1+P\chi e^{-\frac{\omega}{k_BT}}}{1-P\chi e^{-\frac{\omega}{k_BT}}}\right) \tag{42}$$

Multiple Adsorption Model (*1*)

Next we generalize the Langmuir partition function for the case that the lattice can accommodate any integer number of adsorbate molecules on each binding site. An underlying approximation is going to be that the binding sites are all equivalent, though they might take on them different numbers of particles. In order to do so, we will start by generalizing the Langmuir partition function. As seen above, the Langmuir partition function is given by

$$Z(T) = \frac{M!(Q_1(T))^N}{N!(M-N)!} \tag{43}$$

where the subscript 1 indicates that the binding site takes exactly one adsorbate molecule. On the other hand, if the binding site takes no adsorbate molecule, the respective partition function is $Q_0(T) = 1$. The total number of binding sites occupied (by one adsorbate molecule) is given by M_1 whereas the total of unoccupied binding sites is given by $M_0 = M - M_1$. The Langmuir partition function can then be rewritten as and then generalized to

$$Z(T) = \frac{M!(Q_0(T))^{M_0}(Q_1(T))^{M_1}}{M_0!M_1!} = M!\prod\nolimits_i \frac{(Q_i(T))^{M_i}}{M_i!} \tag{44}$$

From the above definitions, it is clear that $M = M_0 + M_1 = \sum_j M_k$ and also that $N = 0{\times}M_0 + 1{\times}M_1 = \sum_j j{\times}M_j$. Furthermore, since the M_j depend on the two independent variables, we can perform a change of variable and write $Z(M_0, M_1, ..., M_{n_{max}}, T)$ instead of $Z(M, N, T)$, where n_{max} denotes the maximum occupation number allowed for the binding sites.

The problem with this change of variable is that we cannot know *a priori* how many binding sites are occupied with s adsorbate molecules. One must thus build a grand-canonical ensemble to treat the system. The grand-canonical partition function can be obtained by averaging the partition functions for different occupation numbers on the binding sites.

$$\Xi(M,T) = \sum\nolimits_N Z(M,N,T) e^{\frac{N\mu}{k_B T}} \tag{45}$$

Note that on the expression above we average only over the occupation numbers of the binding sites and not over the number of binding sites available as well. With some manipulation of the previous expression we arrive at

$$\Xi(M,T) = \sum\nolimits_N M!\prod\nolimits_j \frac{(Q_j(T))^{M_j}}{M_j!} e^{\frac{jM_j\mu}{k_B T}} = \sum\nolimits_N M!\prod\nolimits_j \frac{\left[Q_j(T) exp\left(\frac{j\mu}{k_B T}\right)\right]^{M_j}}{M_j!} \tag{46}$$

Since the main sum goes over all the M_i restricted to the condition $M = \sum_i M_i$ then we can directly apply the multinomial theorem to write

$$\Xi(M,T) = \left[\sum\nolimits_j Q_j(T) exp\left(\frac{j\mu}{k_B T}\right)\right]^M = \xi(T,\mu)^M \tag{47}$$

The grand-canonical partition function can then be written as a linear combination of the partition functions of sites with j adsorbed particles on them. The total amount of sites with j molecules adsorbed forms in this case a subsystem. The chemical potential and temperature for each subsystem are dictated by the surrounding gas phase they are in equilibrium with.

If we furthermore define $\xi(T,\mu)$ as the partition function associated with a particular type of binding site (that can adsorb up to n_{max} gas molecules per binding site) we can further generalize our model to include several types of binding sites by assigning to each binding site its own partition function. If the subsystems composed by different types of binding sites are independent from one another, then the general grand-canonical partition function is

$$\Xi(M,T) = \prod\nolimits_j (\xi_j(T,\mu))^{M_j} \tag{48}$$

One may now ask the question, how many molecules are in average adsorbed by each type of binding site. For simplicity we will only consider one type of binding site, for which $\bar{\theta}$ is the average number of adsorbed molecules. Then for this (sub)system we may write

$$\bar{\theta} = \frac{\sum_j j Q_j(T) exp\left(\frac{j\mu}{k_B T}\right)}{\sum_j Q_j(T) exp\left(\frac{j\mu}{k_B T}\right)} = \frac{\sum_j j Q_j(T)\lambda}{\xi(T,\mu)} = \lambda\left(\frac{\partial log\xi}{\partial\lambda}\right)_T \tag{49}$$

Since $\bar{n}$ is an average occupation number per binding site, then $\bar{\theta} = \frac{\bar{N}}{M}$ and we obtain

$$\bar{N} = M\lambda\left(\frac{\partial log\xi}{\partial\lambda}\right)_T \tag{50}$$

Since $\bar{N}$ defines how many molecules are in average adsorbed, it can be used to describe the adsorption isotherm if we know the partition functions and if we know the maximum number of molecules that can get adsorbed on the surface.

A special case of what was treated above is the case of a linear array of independent pairs of binding sites.

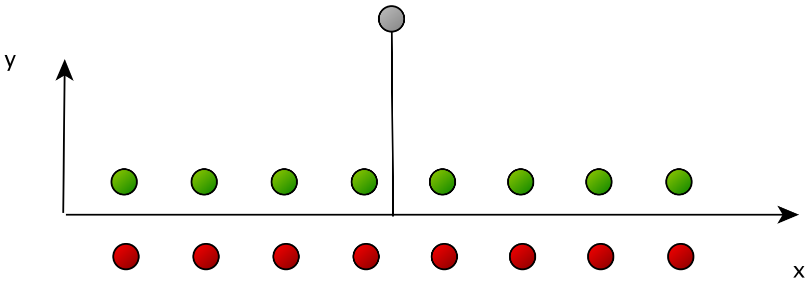

Figure 3: Interaction of a gas molecule with a linear array of pairs of independent binding sites.

Since the sites differ we require two types of partition function: Q_1 is describing the interaction of the adsorbate with binding site type 1 and Q_2 the respective interaction with binding site type 2. We can furthermore assume that whenever both binding sites of a pair are occupied, then bound molecules can interact with interaction energy ω. However, molecules on different pairs will not interact with one another, making different binding pairs independent of one another. If we assume that each binding site can at most bind one adsorbate molecule, then we write

$$\xi(T) = 1 + (Q_1 + Q_2)\,\lambda + Q_1 Q_2 \lambda^2 e^{-\frac{\omega}{k_B T}} \tag{51}$$

The fraction of occupied binding sites is then

$$\bar{\theta} = \frac{(Q_1 + Q_2)\,\lambda + 2Q_1 Q_2 \lambda^2 e^{-\frac{\omega}{k_B T}}}{1 + (Q_1 + Q_2)\,\lambda + Q_1 Q_2 \lambda^2 e^{-\frac{\omega}{k_B T}}} \tag{52}$$

To get the adsorption isotherm we need to make use of the equilibrium condition, which is the equivalence of chemical potentials. Once again we make $\lambda = Pexp\left(\frac{\mu^{0,gas}}{k_B T}\right)$ which yields

$$\bar{\theta} = \frac{(Q_1 + Q_2)\,Pexp\left(\frac{\mu^{0,gas}}{k_B T}\right) + 2Q_1 Q_2 P^2 exp\left(\frac{2\mu^{0,gas}}{k_B T}\right) e^{-\frac{\omega}{k_B T}}}{1 + (Q_1 + Q_2)\,Pexp\left(\frac{\mu^{0,gas}}{k_B T}\right) + Q_1 Q_2 P^2 exp\left(\frac{2\mu^{0,gas}}{k_B T}\right) e^{-\frac{\omega}{k_B T}}} \tag{53}$$

and if like before we define $\chi_i = Q_i exp\left(\frac{\mu^{0,gas}}{k_B T}\right)$ we arrive at

$$\bar{\theta} = \frac{(\chi_1 + \chi_2)\,P + 2\chi_1 \chi_2 P^2 e^{-\frac{\omega}{k_B T}}}{1 + (\chi_1 + \chi_2)\,Pexp\left(\frac{\mu^{0,gas}}{k_B T}\right) + \chi_1 \chi_2 P^2 e^{-\frac{\omega}{k_B T}}} \tag{54}$$

which is the adsorption isotherm.

Next we will consider the the case of M independent, distinguishable and equivalent sites on which an indefinite number of adsorbate molecules may vertically pile upon. Let also Q_i be the partition function for the interaction of a molecule on the i^{th} layer with the lattice. Then we write

$$\xi(T) = \sum\nolimits_{j=1}^{\infty}\prod\nolimits_{k=0}^{j} Q_k \lambda^j \tag{55}$$

with $Q_0 = 1$. With the method described in the current section we write

$$\bar{\theta} = \frac{Q_1\lambda + 2Q_1Q_2\lambda^2 + 3Q_1Q_2Q_3\lambda^3 + ...}{1 + Q_1\lambda + Q_1Q_2\lambda^2 + Q_1Q_2Q_3\lambda^3 + ...} \tag{56}$$

For simplicity we will assume that partition functions for molecules on layers above the first one are all alike, *i.e.* $Q_k = Q_2, k > 1$. Then

$$\begin{aligned}\bar{\theta} &= Q_1\lambda\frac{1 + 2Q_2\lambda + 3Q_2^2\lambda^2 + ...}{1 + Q_1\lambda\left(1 + Q_2\lambda + Q_2^2\lambda^2 + ...\right)} = Q_1\lambda\frac{\sum\nolimits_{n=1}^{\infty} n(Q_2\lambda)^{n-1}}{1 + Q_1\lambda\sum\nolimits_{n=0}^{\infty}(Q_2\lambda)^n} \\ &= Q_1\lambda\frac{\frac{d}{d(Q_2\lambda)}\left[\sum\nolimits_{n=0}^{\infty}(Q_2\lambda)^n - 1\right]}{1 + \frac{Q_1\lambda}{1-Q_2\lambda}} = Q_1\lambda\frac{\frac{d}{d(Q_2\lambda)}\frac{1}{1-Q_2\lambda}}{1 + \frac{Q_1\lambda}{1-Q_2\lambda}} = \frac{\frac{Q_1\lambda}{1-Q_2\lambda^2}}{1 + \frac{Q_1\lambda}{1-Q_2\lambda}}\end{aligned} \tag{57}$$

which we can rearrange to yield

$$\bar{\theta} = \frac{\frac{Q_1}{Q_2}Q_2\lambda}{(1 - Q_2\lambda)(1 - Q_2\lambda + Q_1\lambda)} = \frac{cx}{(1 - x)(1 - x + cx)} \tag{58}$$

where $c = \frac{Q_1}{Q_2}$ and $x = Q_2\lambda$. This is the well known Brunauer-Emmet-Teller equation. The figure below shows the typical behaviour of the BET adsorption isotherm. Note that the larger c is, the larger Q_1 is over Q_2, meaning that the more differential the adsorption on different layers becomes: for larger c, adsorption on the first layer is significantly stronger than adsorption on the second or higher layers. This accounts for the typical behaviour observed on these adsorption isotherms.

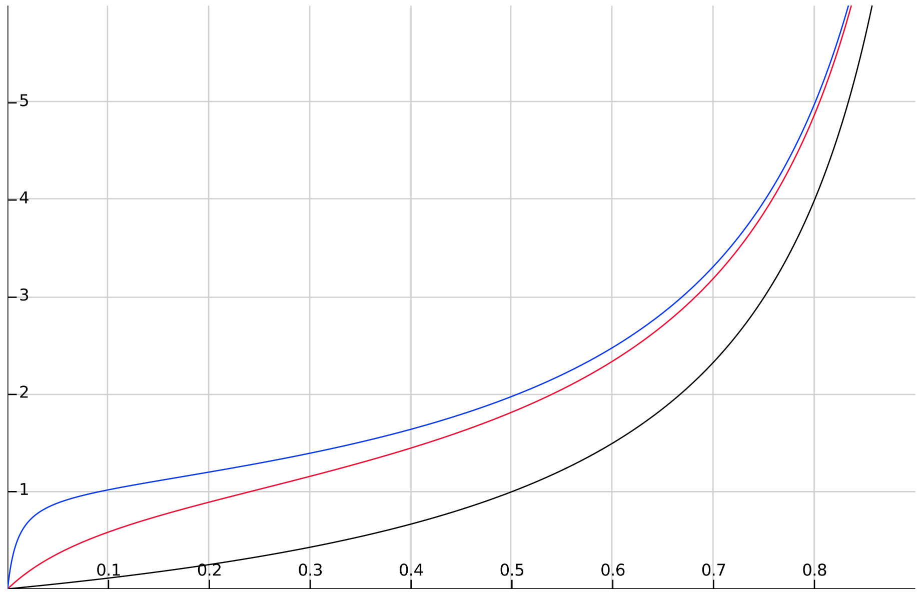

Figure 4: Brunauer-Emmet-Teller curve for three different values of c: 1 (black), 10 (red) and 100 (blue). Plot generated using fooplot (*2*).

One can still use the current formalism to calculate the surface pressure ϕ or the equation of state, which is given by

$$\frac{\phi}{k_B T} = log\xi = log\left(1 + \frac{Q_1\lambda}{1 - Q_2\lambda}\right) = log\left(\frac{1 - Q_2\lambda + Q_1\lambda}{1 - Q_2\lambda}\right) = log\left(\frac{1 - x + cx}{1 - x}\right) \quad (59)$$

According to the above equation, if $x \rightarrow 1$ then the surface pressure ϕ blows off to ∞, which can also be seen graphically in the picture above. This is a big fault of the BET isotherm, since pressure should always remain finite.

Competitive Adsorption (*1*)

The method so far developed can furthermore be used to treat competitive adsorption, where different adsorbate molecules may bind to an adsorbing surface. The simplest case that can be treated is for two types of adsorbate that can bind to equivalent pairs of sites. If each site can bind at most one molecule, then we can define six different partition functions. When no particle is bound to any site, then

$$Q(0, 0) = 1 \quad (60)$$

If however one particle is binding to a binding site we have

$$Q(1, 0) = 2Q_A \quad (61)$$

and

$$Q(0,1) = 2Q_B \tag{62}$$

Note the factor of two that is required since there are two binding sites. Finally, if two particles are bound to the adsorbent

$$Q(2,0) = Q_A^2 exp\left(-\frac{w_{AA}}{k_B T}\right) \tag{63}$$

$$Q(0,2) = Q_B^2 exp\left(-\frac{w_{BB}}{k_B T}\right) \tag{64}$$

$$Q(1,1) = Q_A Q_B exp\left(-\frac{w_{AB}}{k_B T}\right) \tag{65}$$

The grand-canonical partition function is then

$$\begin{aligned} \Xi(M,T) = \xi^M(T) = \left(\sum\nolimits_{s_A}\sum\nolimits_{s_B} Q(s_A,s_B)\lambda_A^{s_A}\lambda_B^{s_B}\right)^M \\ = \big(Q(0,0) + Q(1,0)\lambda_A + Q(0,1)\lambda_B + Q(2,0)\lambda_A^2 + Q(0,2)\lambda_B^2 + Q(1,1)\lambda_A\lambda_B\big)^M \end{aligned} \tag{66}$$

From this we can calculate the average occupation by adsorbate A

$$\bar{\theta}_A = \frac{\lambda_A Q(1,0) + 2Q(2,0)\lambda_A^2 + Q(1,1)\lambda_A\lambda_B}{\xi} \tag{67}$$

and similarly for adsorbate B. Since both gases are in equilibrium with the surface, then

$$\lambda_i = e^{\frac{\mu_i}{k_B T}} = e^{\frac{\mu_i^0}{k_B T}} P_i \tag{68}$$

which yields

$$\bar{\theta}_A = \frac{e^{\frac{\mu_A^0}{k_B T}} P_A Q(1,0) + 2Q(2,0) e^{\frac{2\mu_A^0}{k_B T}} P_A^2 + Q(1,1) e^{\frac{\mu_A^0}{k_B T}} P_A e^{\frac{\mu_B^0}{k_B T}} P_B}{\xi} \tag{69}$$

and

$$\begin{aligned} \xi(T) = Q(0,0) + Q(1,0) e^{\frac{\mu_A^0}{k_B T}} P_A + Q(0,1) e^{\frac{\mu_B^0}{k_B T}} P_B + Q(2,0) e^{\frac{2\mu_A^0}{k_B T}} P_A^2 \\ + Q(0,2) e^{\frac{2\mu_B^0}{k_B T}} P_B^2 + Q(1,1) e^{\frac{\mu_A^0}{k_B T}} P_A e^{\frac{\mu_B^0}{k_B T}} P_B \end{aligned} \tag{70}$$

If once more we use the definition for χ_i in equation 11, then we obtain

$$\bar{\theta}_A = \frac{P_A\chi_A + 2P_A^2\chi_A^2 + P_A\chi_A P_B\chi_B}{1 + P_A\chi_A + P_B\chi_B + P_A^2\chi_A^2 + P_B^2\chi_B^2 + P_A\chi_A P_B\chi_B} \tag{71}$$

which is the adsorption isotherm.

Binding to Non-fixed Matrix (*1*)

One can furthermore consider the binding to a non-fixed or mobile matrix. This particular case is typical for adsorption to macromolecules, dust particles or even in titration problems.

The subsystem one has to look at consists in one adsorbent particle and possibly s bound adsorbate molecules, in which s takes values between 0 and s_{max}. We still assume that the internal degrees of freedom of adsorbent and adsorbate are unaffected by the presence of each other in the interactions taking place. This means rotations, vibrations and electronic properties of both species. The gas is furthermore assumed ideal. Interactions between adsorbate particles can be considered whenever these are bound to the adsorbent. However, interactions between adsorbent particles are always neglected. The system to study can then be schematized by

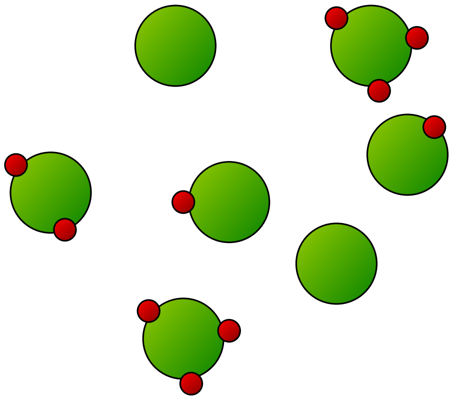

Figure 5: Interaction of an adsorbate with a mobile adsorbing matrix.

For convenience free gas particles are excluded from the treatment. We will therefore consider M adsorbent particles contained in a volume V. On each adsorbent there will be s adsorbate particles adsorbed. In total there will be N adsorbate particles in the system. We let $Q(s)$ be the partition function of the adsorbent with s adsorbed particles on it. This partition function includes not only the interaction between adsorbate and adsorbent, it includes translation, rotation, vibration and electronic contributions. $Q(S)$ includes therefore ideal contributions (proportional to the system's volume) as well as configurational corrections for distributing s particles over m sites. We can furthermore define the quocient $\frac{Q(s)}{Q(0)}$, which refers solely to adsorbate particles. The partition function in the canonical ensemble is given by

$$Z(M_0, M_1, ..., s_{max}, T) = \frac{Q^{M_0}(0)}{M_0!}\frac{Q^{M_1}(1)}{M_1!}...\frac{Q^{s_{max}}(s_{max})}{s_{max}!} \tag{72}$$

Since the number of adsorbed particles is variable, then the most adequate description is done with a grand-canonical partition function:

$$\begin{aligned}\Gamma(M, V, \mu, T) = exp\left(\frac{PV - \mu M}{k_B T}\right) &= \sum\nolimits_{N=0}^{mM} \frac{Q^{M_0}(0)}{M_0!}\frac{Q^{M_1}(1)}{M_1!}...\frac{Q^{s_{max}}(s_{max})}{s_{max}!}\lambda^N \\ = \sum\nolimits_{N=0}^{mM}\prod\nolimits_{i=0}^{s_{max}}\frac{[Q(i)\lambda^i]^{M_i}}{M_i!} &= \sum\nolimits_{N=0}^{mM} Q^M(0)\prod\nolimits_{i=0}^{s_{max}}\frac{\left[\frac{Q(i)}{Q(0)}\lambda^i\right]^{M_i}}{M_i!} \\ = \sum\nolimits_{N=0}^{mM} Q^M(0)\prod\nolimits_{i=0}^{s_{max}}\frac{[Q_0(i)\lambda^i]^{M_i}}{M_i!} &= \frac{Q^M(0)}{M!}\xi^M\end{aligned} \tag{73}$$

where we define

$$\xi = \sum\nolimits_{j=0}^{m} Q_0(j)\lambda^j \tag{74}$$

Note that Γ is not truly a grand-canonical partition function since it is only open with respect to the number of gas molecules and not on the number of sites.

Since $Q(0)$ is only a function of volume and temperature, then the $Q_0(j)$ remain only functions of the temperature. Therefore, ξ is a function of temperature and chemical potential. Once more we can ask the same question, of how many molecules are in average adsorbed.

$$\begin{aligned}\bar{N} = \frac{\sum_N NQ\lambda^N}{\sum_N Q\lambda^N} &= \lambda\left(\frac{\partial log\Gamma}{\partial\lambda}\right)_{M,V,T} \\ = \lambda\left(\frac{\partial log\left[\frac{Q^M(0)}{M!}\xi^M\right]}{\partial\lambda}\right)_{M,V,T} &= \lambda M\left(\frac{\partial log\xi}{\partial\lambda}\right)_{M,V,T}\end{aligned} \tag{75}$$

We can thus conclude that the number of adsorbed molecules depends only on the nature of the interaction between the adsorbate and the adsorbent and not whether the sites are mobile or still.

If however we need to keep the system open also to adsorbate particles we can then write a truly grand-canonical partition function

$$\begin{aligned}\Xi(V, \mu, \mu', T) &= \sum\nolimits_{N,M} Z(N, M, V, T)\lambda^N\lambda'^M \\ &= \sum\nolimits_{M=0}^{+\infty}\frac{Q^M(0)\xi^M\lambda'^M}{M!} = exp\left(Q(0)\xi\lambda'\right)\end{aligned} \tag{76}$$

Once more we can ask the same question, of how many sites are in average occupied:

$$\bar{N} = \lambda \frac{\partial log \Xi}{\partial \lambda} = Q(0)\lambda\lambda' \left(\frac{\partial \xi}{\partial \lambda}\right)_T = \bar{M}\lambda \left(\frac{\partial log \xi}{\partial \lambda}\right)_T \tag{77}$$

which is identical to the equation previously obtained. The results in this case are then in good agreement with what was obtained in previous sections.

Bibliography

1. T. L. Hill, *An Introduction to Statistical Thermodynamics.* Dover, 1986.
2. D. Venkatraman. http://www.fooplot.com. Last checked, 6 May 2020.
3. S. Grimme, J. Antony, S. Ehrlich, and H. Krieg *J. Chem. Phys.*, vol. 132, p. 154104, 2010.
4. E. Caldeweyher, C. Bannwarth, and S. Grimme *J. Chem. Phys.*, vol. 147, p. 034112, 2017.
5. E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth, and S. Grimme *J. Chem. Phys.*, vol. 150, p. 154122, 2019.
6. A. Kundu, G. M. Piccini, K. Sillar, and J. Sauer *J. Am. Chem. Soc.*, vol. 138, p. 14047, 2016.
7. E. Keszei, *Chemical Thermodynamics: An Introduction.* Springer, 2012.
8. T. J. H. Vlugt, R. Krishna, and B. Smit *J. Phys. Chem. B*, vol. 103, p. 1102, 1999.
9. K. Sillar and J. Sauer *J. Am. Chem. Soc.*, vol. 134, p. 18354, 2012.