

The Langmuir Isotherm and the Fermi Distribution Are One and the Same Expression

— Change the Variable and the Difference Becomes 0 — Not the Same Rhyme but the Same Root, and That Root Is “A Site Takes Only 0 or 1” — [Paper 284]

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— *From thinking to syncing.* —

Abstract

The Langmuir adsorption isotherm of surface chemistry $\theta = Kp/(1 + Kp)$, the Fermi distribution of solid-state physics $f = 1/\{1 + e^{(E-\mu)/kT}\}$, and the Michaelis–Menten expression of enzyme kinetics $v/V_{\max} = [S]/(K_m + [S])$ —these three share a form. This paper asks whether that is an accidental likeness (a rhyme) or the same root—the answer is the same root. No new mathematical theorem and no new law is claimed. First, changing the variable makes the difference 0. Setting $Kp = e^{(\mu-E)/kT}$, the difference at five points is 0 or below 10^{-16} (Section 2). Second, this is the core of the paper. The root is that one site takes only 0 or 1, and if the exclusion is the same, the distribution is the same (Section 3). Third, the fuller the sites, the less it acts. Raising θ from 0.9 to 0.99 takes 11 times the pressure; from 0.5 to 0.999 it takes 999 times (Section 4). Fourth, the first half is symmetric. Both $0.1 \rightarrow 0.5$ and $0.5 \rightarrow 0.9$ take exactly 9 times (Section 4). Fifth, the same 11 appears on the Michaelis side. Raising $v/V_{\max}$ from 0.9 to 0.99 takes 11 times the substrate concentration (Section 5). Sixth, the separator is whether the number of sites is finite. The Freundlich expression does not saturate, and the BET expression diverges as $\theta \rightarrow \infty$ (Section 6).

Scope of this paper (scope note): No new mathematical theorem and no new law is claimed—the Langmuir, Fermi–Dirac, Michaelis–Menten, Freundlich and BET expressions are all standard. We do not build statistical mechanics—all we use is one change of variable and one division. We do not derive the Fermi distribution—we do not enter the derivation from the grand canonical ensemble. We do not discuss the mechanism of adsorption—heat of adsorption, surface diffusion, and the distinction between chemisorption and physisorption are not treated at all. We do not discuss enzyme mechanism—the Michaelis–Menten expression follows from a steady-state approximation, and the validity of that approximation is not treated. Only the agreement of form is treated. We do not say the three are “the same phenomenon”—what agrees is the form of the distribution function, not the phenomena. The Fermi distribution comes from quantum statistics, Langmuir from an equilibrium constant, Michaelis from reaction rates: the routes of derivation differ. The Michaelis root is weaker—the agreement of Langmuir and Fermi rests on the same root, exclusion, whereas the Michaelis “site” is the separate circumstance that one enzyme molecule binds one substrate. This paper does not claim it as a third case of the same root, and keeps it to the agreement of form. Relation to earlier papers: Paper 112 counted “six distinct roots sharing one rhyme”—this paper is the converse case, an example where not only the rhyme but the root is the same. It is set as the counterpart to 112. Paper 265 showed that what separated the low-temperature models is the density of states—this paper is on the distribution-function side and does not treat the density of states. Paper 274 showed that Drude was right through the cancellation of two errors—the agreement here is not a cancellation but an identity. Paper 220 counted four things called “independence”—the “exclusion” there is the mutual exclusivity of probabilistic events, a different thing from the exclusion of sites here. What is added is confirming at five points that a change of variable makes the difference between the two expressions 0, naming the root as exclusion, confirming that $0.1 \rightarrow 0.5$ and $0.5 \rightarrow 0.9$ both take 9 times, and separating the three expressions by the presence or absence of saturation.

1. Lining Up the Three Expressions

We line up three expressions from different fields, harmonising only the symbols.

Field	Expression	Variables
Surface chemistry (Langmuir)	$\theta = \frac{Kp}{1 + Kp}$	θ coverage, p pressure
Solid-state physics (Fermi)	$f = \frac{1}{1 + e^{(E-\mu)/kT}}$	f occupancy, E energy
Enzyme kinetics (Michaelis)	$\frac{v}{V_{\max}} = \frac{[S]}{K_m + [S]}$	v rate, $[S]$ substrate

Observation 1.1

All three have the form $\frac{x}{1+x}$. The first row has $x = Kp$ and the third $x = [S]/K_m$ —only the second does not look like it.

Question: Is this an accidental likeness or the same root?

2. Change the Variable and the Difference Becomes 0

Setting: We try to put the Fermi distribution into the form $\frac{x}{1+x}$.

$$f = \frac{1}{1 + e^{(E-\mu)/kT}} = \frac{e^{(\mu-E)/kT}}{e^{(\mu-E)/kT} + 1}$$

So setting $Kp = e^{(\mu-E)/kT}$, the two expressions are literally the same.

Check 2.1: We match the numbers at five points.

$(E - \mu)/kT$	Langmuir	Fermi	Difference
−4	0.9820137900	0.9820137900	0
−2	0.8807970780	0.8807970780	1.11×10^{-16}
0	0.5000000000	0.5000000000	0
+2	0.1192029220	0.1192029220	0
+4	0.0179862100	0.0179862100	3.47×10^{-18}

Observation 2.2

The difference is **0**, or the size of machine rounding. They are not close but the same—the two expressions are one expression whose variables carry different names.

Check 2.3: We write out the corresponding variable values.

Kp	θ	Corresponding $(E - \mu)/kT$
0.01	0.009901	+4.6052
0.10	0.090909	+2.3026
1.00	0.500000	0
9.00	0.900000	-2.1972
99.00	0.990000	-4.5951

Observation 2.4

$Kp = 1$ corresponds to $E = \mu$. The chemical condition “pressure exactly the reciprocal of the equilibrium constant” and the physical condition “energy exactly at the chemical potential” are the same point——both are half filled.

3. The Core: The Root Is That a Site Takes Only 0 or 1

Setting: We ask why they agree. The manipulation shows the agreement but does not explain it.

Observation 3.1

Their derivations share one line.

States one site can take	
Langmuir adsorption	empty, or one molecule $\Rightarrow \{0, 1\}$
Fermi distribution	empty, or one electron (Pauli) $\Rightarrow \{0, 1\}$

Observation 3.2

This is the core of the paper. The grand partition function of one site is $\Xi = 1 + e^{(\mu - E)/kT}$ in both cases——the sum stops at exactly two terms, so the mean occupancy is $\frac{e^{(\mu - E)/kT}}{1 + e^{(\mu - E)/kT}}$.

Observation 3.3

If the exclusion is the same, the distribution is the same. The adsorbed molecule need not be an electron, and no Pauli principle need be acting——what is needed is only the one line “a site accepts only one”.

Observation 3.4

Paper 112 counted “six distinct roots sharing one rhyme.” This paper is its counterpart——here not only the rhyme but the root is the same, and that is why the difference is 0.

Observation 3.5

A point to write honestly——the Michaelis–Menten expression is not this strong. What plays the role of the “site” is an enzyme molecule binding one substrate, arrived at through the separate premise of a steady-state approximation——this paper does not claim the third as “the same root” and keeps it to agreement of form.

4. The Fuller the Sites, the Less It Acts

Setting: How many times the pressure does it take to raise θ from θ_1 to θ_2 ? Since $Kp = \theta/(1 - \theta)$, the ratio is $\frac{\theta_2(1 - \theta_1)}{\theta_1(1 - \theta_2)}$.

Check 4.1:

Change in θ	Factor in pressure required
0.1 $\rightarrow$ 0.5	9.0000
0.5 $\rightarrow$ 0.9	9.0000
0.9 $\rightarrow$ 0.99	11.0000
0.99 $\rightarrow$ 0.999	10.0909
0.5 $\rightarrow$ 0.99	99.0000
0.5 $\rightarrow$ 0.999	999.0000

Observation 4.2

0.1 $\rightarrow$ 0.5 and 0.5 $\rightarrow$ 0.9 both take exactly 9. It is symmetric about $\theta = 0.5$ —because the expression is preserved under $\theta \rightarrow 1 - \theta$, $Kp \rightarrow 1/(Kp)$.

Observation 4.3

Above 0.9 the factor rises (to 11). Higher still it approaches 10.09—cutting the remaining sites by one order costs one order of pressure.

Observation 4.4

Going from 0.5 to 0.999 takes **999** times. The first half needed only $Kp = 1$, yet the last 0.499 needs 999 times—the price of the number of sites being finite.

5. The Same 11 Appears on the Michaelis Side

Check 5.1: We ask the same question for the enzyme. How many times the substrate concentration does it take to raise $v/V_{\max}$?

$v/V_{\max}$	$[S]$ required	Factor
0.5	$1.0K_m$	—
0.9	$9.0K_m$	9
0.99	$99.0K_m$	11

Observation 5.2

The **11** comes out as it is. This is expected since the expression is the same, but that it is expected is the point of this paper—numerical intuition earned in adsorption transfers unchanged to enzymes.

Observation 5.3

The meaning of K_m sits in the same place. $[S] = K_m$ gives half—the same point as Langmuir’s $Kp = 1$ and Fermi’s $E = \mu$.

6. Separator: Whether the Number of Sites Is Finite

Observation 6.1

Separator—what must be moved for this form to become another? Whether the number of sites is finite.

Check 6.2: We compare with three expressions that do not saturate.

Expression	Behaviour at high pressure	Number of sites
Langmuir $\theta = \frac{Kp}{1 + Kp}$	$\theta \rightarrow 1$	finite (monolayer)
Freundlich $\theta \propto p^{1/n}$	$\theta \rightarrow 10^{6/n}$ at $p = 10^6$ (diverges)	heterogeneous, unbounded
BET (multilayer)	$\theta \rightarrow \infty$ as $p \rightarrow p_0$	layers stack

Observation 6.3

With $n = 1$, Freundlich returns $\theta = 10^6$ at $p = 10^6$. Since coverage exceeds 1, the monolayer picture has been abandoned—it fails to saturate not because the approximation is poor but because it is not counting sites.

Observation 6.4

Hence whether an expression has this form is not settled by field. Within surface chemistry itself, Langmuir has it while Freundlich and BET do not—what separates them is only the one line “is a site 0 or 1”.

Observation 6.5

The agreement of the Drude model treated in Paper 274 was a cancellation of two errors. The agreement here is not a cancellation—it is an identity, with the difference going to 0 under a change of variable. The same “fits well” has a different standing.

7. Roll Call and Closing

1. All three are $x/(1+x)$ (Observation 1.1): Only Fermi does not look it.
2. Difference 0 under a change of variable (Check 2.1): All five points below 10^{-16} .
3. $Kp = 1$ is $E = \mu$ (Check 2.3): Both half filled.
4. The root is exclusion (Observation 3.2): $\Xi = 1 + e^{(\mu-E)/kT}$ stops at two terms.
5. The counterpart to 112 (Observation 3.4): Not the rhyme but the root.
6. $0.1 \rightarrow 0.5$ and $0.5 \rightarrow 0.9$ both 9 (Check 4.1): Symmetric about a half.
7. $0.9 \rightarrow 0.99$ is 11 (Check 4.1): The fuller, the less it acts.
8. $0.5 \rightarrow 0.999$ is 999 (Check 4.1): The first half needed 1.
9. Michaelis gives 11 too (Check 5.1): Intuition transfers unchanged.
10. Freundlich gives $\theta = 10^6$ (Check 6.2): It is not counting sites.

Closing: The Langmuir isotherm and the Fermi distribution are not alike; they are one and the same expression. Merely setting $Kp = e^{(\mu-E)/kT}$ makes the difference at all five points 0 or the size of rounding. The root is one line—a single site takes only 0 or 1. So the grand partition function stops at two terms, and if the exclusion is

the same the distribution is the same. Numerical intuition transfers unchanged—the **11** times the pressure needed to raise θ from 0.9 to 0.99 is the same number as the **11** times the substrate needed to raise $v/V_{\max}$ from 0.9 to 0.99. And $0.1 \rightarrow 0.5$ and $0.5 \rightarrow 0.9$ both take exactly **9**—symmetric about a half. One thing separates them—whether the number of sites is finite. If it is, this form follows; if not, it diverges as Freundlich and BET do. Not the field. Where Paper 112 counted six distinct roots under one rhyme, here the root is the same as well, and that is why the difference is 0.

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