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Stochastic Model for Langmuir Isotherm

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A monolayer adsorption isotherm was deduced theoretically by Langmuir on the basis of a kinetic interpretation of the adsorption of gas molecules on a solid surface.[1] On the same assumption as in the classical Langmuir theory, a stochastic model for the adsorption-desorption process in a closed system at constant temperature can be formulated as follows. Let us denote by $p(n)$ the probability of finding n adsorbed molecules in stationary state and by λ and μ the probabilities of adsorption and desorption for one molecule, respectively. The probability $p(n)$ then satisfies the set of difference equations,[2]

$$\lambda\{\gamma-(n-1)\}\{(\sigma-(n-1)\}p(n-1)-\{\lambda(\gamma-n)(\sigma-n)+\mu n\}p(n)+\mu(n+1)p(n+1)=0 \quad (0\leq n\leq\sigma) \tag{1}$$

where γ is the total number of molecules in the system under consideration, σ the number of sites on the surface and $\gamma>\sigma$ and $p(-1)=p(\sigma+1)=0$ have been assumed. The probability $p(n)$ is independent of the initial state of the system and $\sum_{n=0}^{\sigma}p(n)=1$ is satisfied. The set of difference equations, (1), may be solved recurrently. We then have the stationary probability distribution,

$$p(n)=r_n z^n/R_{\sigma,\gamma}(z) \tag{2}$$

where $z=\lambda/\mu$ and $r_n=\binom{\sigma}{n}(\gamma)_n=\binom{\sigma}{n}\gamma!/(\gamma-n)!$ and $R_{\sigma,\gamma}(z)=\sum_{n=0}^{\sigma}r_n z^n$ is called the rook polynomial.[3] The probability distributions for different values of z are illustrated in Fig. 1. It is to be noted, here, that the statistic-mechanical model leads also to the probability distribution,[4]

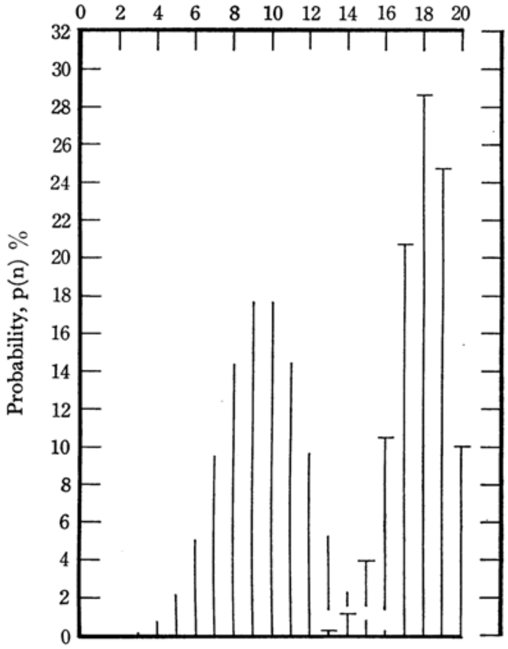

Fig. 1. Probability distribution.
$\gamma=100$, $\sigma=20$; —: $z=10^{-2}$, |—: $z=10^{-1}$

$$p_{\text{S.M.}}(n)=(1/Q)\frac{\sigma!}{n!(\sigma-n)!}q^n\frac{1}{(\gamma-n)!}q_G{}^{\gamma-n} = (q_G{}^{\gamma}/Q\gamma!)\binom{\sigma}{n}(\gamma)_n(q/q_G)^n \tag{3}$$

which is of the same form as (2). In this formula, the quantities q and q_G denote respectively the partition functions of adsorbed and gaseous molecules and the partition function for the whole system,

$$Q=(q_G{}^{\gamma}/\gamma!)\sum_{n=0}^{\sigma}\binom{\sigma}{n}(\gamma)_n(q/q_G)^n$$

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[1] I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916); **40**, 1361 (1918).

[2] K. Ishida, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **81**, 524 (1960).

[3] J. Riordan, "An Introduction to Combinatorial Analysis," John Wiley & Sons, Inc., New York, N. Y. (1958), p. 171.

[4] For proof, refer to T. L. Hill, "Introduction to Statistical Thermodynamics," Addison-Wesley Publishing Company, Reading, Massachusetts (1960), Section 10-3.

is regarded as the normalization factor.

It follows from (2) that the mean number of adsorbed molecules, $\langle n\rangle$, is given by

$$\langle n\rangle = z\frac{\mathrm{d}}{\mathrm{d}z}R_{\sigma,\gamma}(z)/R_{\sigma,\gamma}(z) \tag{4}$$

It is convenient to relate $R_{\sigma,\gamma}(z)$ to the confluent hypergeometric function[5] $\Phi(\gamma+1,\ \gamma-\sigma+1;\ 1/z)$ by the formula,

$$R_{\sigma,\gamma}(z) = (\gamma)_\sigma z^\sigma \mathrm{e}^{-1/z}\,\Phi(\gamma+1,\ \gamma-\sigma+1;\ 1/z) \tag{5}$$

Substituting (5) into (4) and using the differential relation,

$$z\frac{\mathrm{d}}{\mathrm{d}z}\Phi(\gamma+1,\ \gamma-\sigma+1;\ 1/z) = \sigma\Phi(\gamma,\ \gamma-\sigma+1;\ 1/z) - (\sigma+1/z)\,\Phi(\gamma+1,\ \gamma-\sigma+1;\ 1/z)$$

we obtain

$$\langle n\rangle = \sigma\Phi(\gamma,\ \gamma-\sigma+1;\ 1/z)/\Phi(\gamma+1,\ \gamma-\sigma+1;\ 1/z) \tag{6}$$

Therefore, the mean number of gas molecules, $\langle n_G\rangle = \gamma - \langle n\rangle$, is given by

$$\langle n_G\rangle = (\gamma-\sigma)\Phi(\gamma,\ \gamma-\sigma;\ 1/z)/\Phi(\gamma+1,\ \gamma-\sigma+1;\ 1/z) \tag{7}$$

where we have used the recurrence relation,

$$\gamma\Phi(\gamma+1,\ \gamma-\sigma+1;\ 1/z) - \sigma\Phi(\gamma,\ \gamma-\sigma+1;\ 1/z) = (\gamma-\sigma)\,\Phi(\gamma,\ \gamma-\sigma;\ 1/z)$$

It follows from (6) and (7) that the stochastic Langmuir isotherm may be written in the form,

$$\langle n\rangle = \sigma\frac{z\langle n_G\rangle}{1+z\langle n_G\rangle - z(\gamma-\sigma)\Delta} \tag{8}$$

where for brevity we have introduced a quantity Δ defined by

$$\Delta = \Phi(\gamma,\ \gamma-\sigma;\ 1/z)/\Phi(\gamma+1,\ \gamma-\sigma+1;\ 1/z) - \Phi(\gamma-1,\ \gamma-\sigma;\ 1/z)/\Phi(\gamma,\ \gamma-\sigma+1;\ 1/z)$$

In deriving (8), we have also used the recurrence relation,

$$(1/z)\,\Phi(\gamma,\ \gamma-\sigma+1;\ 1/z) = (\gamma-\sigma)\{\Phi(\gamma,\gamma-\sigma;\ 1/z) - \Phi(\gamma-1,\ \gamma-\sigma;\ 1/z)\}$$

It is possible, however, to connect the quantity Δ with the variance (fluctuation),

$$\langle n^2\rangle - \langle n\rangle^2 = \langle n\rangle + z^2\frac{\mathrm{d}^2}{\mathrm{d}z^2}R_{\sigma,\gamma}(z)/R_{\sigma,\gamma}(z) - \left(z\frac{\mathrm{d}}{\mathrm{d}z}R_{\sigma,\gamma}(z)/R_{\sigma,\gamma}(z)\right)^2$$

Applying (5) to this equation, we obtain, after rather long but straightforward algebra,

$$\langle n^2\rangle - \langle n\rangle^2 = \langle n\rangle\,(\gamma-\sigma)\Delta \tag{9}$$

where $\Delta > 0$ in the case of $\gamma > \sigma$. By combining (9) with (8), we obtain

$$\langle n\rangle = \sigma\frac{z\langle n_G\rangle}{1+z\langle n_G\rangle}\left\{1+\frac{\langle n^2\rangle - \langle n\rangle^2}{\sigma\langle n_G\rangle}\right\} \tag{10}$$

which can be also deduced directly from (1). Since the inequality $\langle n^2\rangle - \langle n\rangle^2 \leqslant \sigma\langle n_G\rangle$ holds for ordinary statistical thermodynamic systems, (10) becomes

$$\langle n\rangle \simeq \sigma\frac{z\langle n_G\rangle}{1+z\langle n_G\rangle}$$

which is, in the mean, consistent with the classical Langmuir isotherm. The variance (9), however, may not be negligible in small systems.

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[5] A. Erdélyi *et al.*, "Higher Transcendental Functions," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y. (1953), p. 248.