Equilibrium distribution of gas molecules adsorbed on an active surface

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We evaluate the exact equilibrium distribution of gas molecules adsorbed on an active surface with an infinite number of attachment sites. Our result is a Poisson distribution having mean $X=\mu P P_s/P_e$, with μ the mean gas density, P_s the sticking probability, P_e the evaporation probability in a time interval τ, and P Smoluchowski's exit probability in time interval τ for the surface in question. We then solve for the case of a finite number of attachment sites using the mean field approximation, recovering the Langmuir isotherm in this case.

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I. INTRODUCTION

One of the models aimed at explaining the collapse of the wave function [1] predicts that the wave function of every system collapses to an eigenstate of the Hamiltonian in the energy basis in a time which depends on the energy spread of the wave packet. For a system including the measuring apparatus, relevant sources of energy fluctuations are thermal energy fluctuations and energy (mass) fluctuations coming from fluctuations in the number of surface adsorbed molecules. Our aim in this paper is to derive formulas for the equilibrium distribution of adsorbed molecules on an active surface *S*, from which the root mean square mass fluctuation can be calculated. Our results could also be relevant in other contexts, e.g., in surface catalysis.

Since our work is based largely on the classical colloidal statistics problem [2] solved by Smoluchowski, we will review his result first. Consider a gas chamber of volume V which has N gas molecules distributed randomly inside. Assuming uniform occupancy, the probability that a single molecule is found inside a small subvolume v is v/V, and that of not being found inside is $(V-v)/V$. Thus the probability $U(n)$ of some n particles being found inside v is given by the binomial distribution

$$U(n)=\binom{N}{n}\left(\frac{v}{V}\right)^n\left(1-\frac{v}{V}\right)^{N-n}. \tag{1}$$

The mean number of particles μ found inside the small volume v is just the mean of this binomial distribution Nv/V. In terms of μ, then, the distribution $U(n)$ becomes

$$U(n)=\binom{N}{n}\left(\frac{\mu}{N}\right)^n\left(1-\frac{\mu}{N}\right)^{N-n}. \tag{2}$$

For most practical cases N and V are both very large, but the ratio of N/V is finite so that the mean μ is finite. In this limit, the binomial distribution of Eq. (2) reduces to the Poissonian form

$$U(n)=\frac{e^{-\mu}\mu^n}{n!}. \tag{3}$$

The interpretation of this equation is the following: If we focus on a small subvolume v inside a much larger volume V, then the frequency with which different numbers of particles will be observed in the smaller volume will follow a Poisson distribution. It should be noted that in addition to the assumption of all positions in the volume having equal *a priori* probabilities of occupancy, we also assume that the motions of individual particles are mutually independent. In the surface adsorption generalization discussed in Sec. II, this is the case for an infinite number of attachment sites, but would not be the case for a finite number of attachment sites.

Let us now define P to be the probability that a particle somewhere inside the small volume v will have emerged from it during the time interval τ. The ''probability aftereffect factor'' P will depend on physical parameters such as the velocity distribution and mean free path of the particles, as well as on the geometry of the surface boundary. In terms of P, the probability that, starting with an initial situation of n molecules inside v, i of them escape in time τ is

$$A(n,i)=\binom{n}{i}P^i(1-P)^{n-i}. \tag{4}$$

Let E_i denote the probability of the volume v capturing i particles during time τ. E_i clearly is independent of the number of molecules already inside. However, under equilibrium conditions, the *a priori* probabilities for an entrance and exit must be equal. For each n there is a contribution to the exit probability; summing over all of them and equating to E_i, we obtain

$$E_i=\sum_{n=i}^{\infty}U(n)A(n,i). \tag{5}$$

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Inserting the expressions for $U(n)$ and $A(n,i)$ from Eqs. (3) and (4), we obtain

$$E_i=\sum_{n=i}^{\infty}\frac{e^{-\mu}\mu^n}{n!}\binom{n}{i}P^i(1-P)^{n-i}$$
$$=\frac{e^{-\mu}(\mu P)^i}{i!}\sum_{n=i}^{\infty}\frac{\mu^{n-i}(1-P)^{n-i}}{(n-i)!}$$
$$=\sigma(i,\mu P), \tag{6}$$

where from here on we denote a Poisson distribution with mean X by $\sigma(n,X)$, with

$$\sigma(n,X)=\frac{e^{-X}X^n}{n!}. \tag{7}$$

II. ADSORPTION OF GAS MOLECULES

To make our analysis intuitively clear, let us draw an imaginary surface I just outside the active surface area S. The following notations will be used: (i) E_i is the probability for i molecules to enter the volume enclosed by I in the time interval τ. Since this is the same as in the case where the surface S inside is absent, this probability is just as in Eq. (6):

$$E_i=\sigma(i,\mu P). \tag{8}$$

(ii) $U(n)$ is the probability to observe n molecules sticking to S. (iii) P_s is the probability of a molecule to stick to S after crossing I. (iv) P_e is the probability for a molecule that is stuck to S to evaporate off in a time interval τ. (v) $B(n,i)$ is the probability that starting with an initial situation with n particles stuck to S, i of them evaporate in time τ.

By Smoluchowski's reasoning, leading to Eq. (4) above, we have

$$B(n,i)=\binom{n}{i}(P_e)^i(1-P_e)^{n-i}. \tag{9}$$

At equilibrium, the detailed balance condition holds. This is just the condition that the probability that i particles stick in a time interval τ is equal to the probability that i particles evaporate in the same time interval τ. The probability for i molecules to stick to S is

$$\sum_{j\geqslant i}E_j\binom{j}{i}P_s^i(1-P_s)^{j-i}. \tag{10}$$

Using Smoluchowski's expression for E_j from Eq. (8), this becomes

$$e^{-\mu P}\frac{(\mu PP_s)^i}{i!}\sum_{j\geqslant i}\frac{[\mu P(1-P_s)]^{j-i}}{(j-i)!}=\sigma(i,\mu PP_s). \tag{11}$$

The other part of the detailed balance condition, the probability that out of n molecules on S, i of them evaporate in time interval τ, is

$$\sum_{n\geqslant i}U(n)B(n,i)=\sum_{n\geqslant i}U(n)\binom{n}{i}P_e^i(1-P_e)^{n-i}. \tag{12}$$

Equating these two probabilities, we have

$$\sigma(i,\mu PP_s)=\sum_{n\geqslant i}U(n)\binom{n}{i}P_e^i(1-P_e)^{n-i}. \tag{13}$$

Our task now is to determine the equilibrium distribution $U(n)$ from this equation. We start with the ansatz that $U(n)$ is a Poisson distribution $\sigma(n,X)$, with a mean X which is to be determined:

$$U(n)=\sigma(n,X)=\frac{e^{-X}X^n}{n!}. \tag{14}$$

Substituting Eq. (7) into Eq. (13), and using the sum evaluated in Eq. (6), we obtain the condition

$$\sigma(i,\mu PP_s)=\sigma(i,XP_e), \tag{15}$$

which is satisfied when

$$X=\frac{\mu PP_s}{P_e}. \tag{16}$$

Equations (14) and (16) are our results for the equilibrium distribution of adsorbed molecules. We note that, as intuitively expected, the mean number of adsorbed molecules increases with increasing gas density μ and increasing sticking probability P_s, but decreases with increasing evaporation probability P_e.

As a check on our reasoning, let us calculate the transition probability $W(n,m)$ for m particles to be stuck to the surface at time $T+\tau$, when n particles were stuck to the surface at time T, and then check that $W(n,m)$ and $U(n)$ have the requisite Markoff property. The transition probability is given by

$$W(n,m)=\sum_{x+y=m}W_1^{(n)}(x)W_2(y), \tag{17}$$

where $W_1^{(n)}(x)$ is the probability that x particles remain at time $T+\tau$ when initially there were n at time T,

$$W_1^{(n)}(x)=\binom{n}{x}(1-P_e)^xP_e^{n-x}, \tag{18}$$

and $W_2(y)$ is the probability for y additional particles to adhere to the surface in time τ as given by Eq. (11):

$$W_2(y)=\sigma(y,\mu PP_s). \tag{19}$$

The Markoff property requires that

$$U(m)=\sum_n U(n)W(n,m), \tag{20}$$

with $U(m)$ the equilibrium distribution of Eqs. (14) and (16). Evaluating the sum on the right-hand side of Eq. (20), we find, as required, that

$$\sum_{x+y=m}\left(\sum_{n} U(n)W_1^{(n)}(x)\right)W_2(y)$$

$$=\sum_{x+y=m}\sigma(x,X(1-P_e))\sigma(y,\mu PP_s)$$

$$=\sigma(m,X(1-P_e)+\mu PP_s)=\sigma(m,X)=U(m). \tag{21}$$

III. FINITE NUMBER OF ATTACHMENT SITES: MEAN FIELD APPROACH

Let us now proceed to calculate the equilibrium distribution of the number of molecules attached to S, where S has a finite (although very large) number of attachment sites M. Clearly, our discussion of Sec. II breaks down, since the sticking probability is no longer a constant, but depends on the number n of molecules already attached to S. In the following discussion, let us use P_s to denote the probability for a molecule to stick to S if no site is occupied, and let us denote the mean number of occupied sites by $\overline{m}$. Then the mean sticking probability is just

$$\overline{P}_s=P_s\left(1-\frac{\overline{m}}{M}\right), \tag{22}$$

and the corresponding distribution of stuck molecules is $\sigma(n,\overline{X})$, with

$$\overline{X}=\frac{\mu P\overline{P}_s}{P_e}. \tag{23}$$

Since the mean of this distribution is $\overline{m}=\overline{X}$, we obtain the mean field consistency condition

$$\overline{m}=\left(1-\frac{\overline{m}}{M}\right)\frac{\mu PP_s}{P_e}, \tag{24}$$

with solution

$$\overline{m}=\frac{\mu PP_s/P_e}{\left(1+\dfrac{\mu PP_s}{P_eM}\right)}. \tag{25}$$

Thus the mean fraction $\overline{m}/M$ of total available sites occupied has the form of the Langmuir isotherm [3].

The mean field approximation is valid as long as the mean number of vacant sites $M-\overline{m}$ is much larger than the width $\sqrt{\overline{m}}$ of the distribution of adsorbed molecules,

$$M-\overline{m}=M\left(1-\frac{\overline{m}}{M}\right)\gg\sqrt{\overline{m}}=\sqrt{M}\left(\frac{\overline{m}}{M}\right)^{1/2}. \tag{26}$$

Close to saturation, when $\overline{m}/M\approx 1$, substituting Eq. (25) into Eq. (26) gives the condition

$$1+\frac{\mu PP_s}{P_eM}\ll\sqrt{M}, \tag{27}$$

which when $X=\mu PP_s/P_e\gg M$ simplifies to

$$X\ll M^{3/2}. \tag{28}$$

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